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Service Life of Concrete

James R. Clifton and Lawrence I. Knab

U.S. DEPARTMENT OF COMMERCE
National Institute of Standards and Technology
National Engineering Laboratory
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U.S. DEPARTMENT OF COMMERCE
Robert Mosbacher, Secretary
NATIONAL INSTITUTE OF STANDARDS
AND TECHNOLOGY
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EXECUTIVE SUMMARY

The U.S. Nuclear Regulatory Commission (NRC) has the responsibility for developing a strategy for storing low-level radioactive waste (LLW). One approach being considered involves storing radioactive wastes in concrete vaults which are either i) buried in the earth or ii) constructed above ground and covered with earth. In either scenario, the vaults will be below the frost line and above the groundwater table. A service life of 500 years is required for the storage vaults. The National Institute of Standards and Technology is carrying out a project for the NRC aimed at determining if concrete can be developed which will have the desired service life. If the results of the project indicate that a 500 year life for concrete is achievable, performance criteria will then be developed to form a technical bases for selecting concrete materials. This report is based on an analysis of the major degradation processes which are likely to effect the performance of the underground storage vaults and on methods for predicting the service life of concrete.

The major degradation processes that concrete of underground vaults will likely encounter are sulfate attack, corrosion of reinforcing steel, alkali-aggregate reactions, and leaching by ground water. Freezing and thawing damage could occur before the vaults are covered with soil and therefore are addressed. Other degradation processes which could occur are microbiological attack, salt crystallization, and attack by LLW, especially acids. All of these processes involve the penetration of the concrete by water or aqueous solutions. Therefore, it is concluded that concrete with low permeabilities are most likely to achieve service lives of around 500 years.

The permeability of concrete is dependent on the porosity and pore structure of the cement matrix, especially the extent of pore interconnectedness. Many factors affect the pore properties of concrete with the water-to-cement ratio having the greatest effect. Cracking also can significantly increase the permeability of concrete and can limit the beneficial effects of producing low water-to-cement concrete.

An approach for predicting the service life of the concrete is presented. It involves the integration of mathematical models and accelerated durability testing. Several models have been reported for predicting the service lives of concrete, including models for concrete exposed to corrosive conditions, freezing and thawing conditions, and to groundwater. However, these models appear to give at the most qualitative estimates of service lives. Further work on the development of models is recommended to form a basis for making reasonable estimate of service lives.

The rates of most of the likely degradation processes can be predicted based on modeling and accelerated testing. An exception is alkali-aggregates reactions. Present test methods are not adequate to predict the behavior of potentially reactive aggregates in field concrete. Furthermore, the present knowledge on alkali-aggregate reactions is inadequate for making service life predictions. It is, therefore, recommended that a test method be developed for determining if an aggregate is potentially reactive. An aggregate would then be accepted or rejected based on its reactivity rather than on its rate of reaction.

The long-term performance of concrete is often controlled by the level of its quality. Based on available knowledge, it seems likely that concrete can be formulated which should have service lives of 500 years in the expected environments. However, such lives will be obtainable only if the concrete materials meet carefully defined specifications, and good construction practices are followed.

ABSTRACT

The U.S. Nuclear Regulatory Commission (NRC) has the responsibility for developing a strategy for the disposal of low-level radioactive waste (LLW). An approach being considered for their disposal is to place the waste forms in concrete vaults buried in the earth. A service life of 500 years is required for the concrete vaults as they may be left unattended for much of their lives.

This report examines the basis for making service life predictions based on accelerated testing and mathematical modeling of factors controlling the durability of concrete buried in the ground. Degradation processes are analyzed based on considerations of their occurrence, extent of potential damage, and mechanisms. A recommended research plan for developing methods for predicting the service life of concrete is presented.

The major degradation processes that concrete of underground vaults will likely encounter are sulfate attack, corrosion of reinforcing steel, alkali-aggregate reactions, and leaching by ground water. Freezing and thawing damage could occur before the vaults are covered with soil and therefore are addressed. Other degradation processes which may occur are microbiological attack, salt crystallization, and attack by LLW, especially by acidic materials. Two important factors controlling the resistance of concrete to these degradation processes are its quality and permeability. Concepts of quality and factors affecting quality of concrete are discussed. Permeability is discussed in terms of the water-to-cement ratio, the pore structure of concrete, and the effects of cracks.

KEYWORDS: Accelerated testing; alkali-aggregate reactions; concrete; corrosion; durability; groundwater; mathematical modeling; permeability; service life; sulfate attack.

Table of Contents

	<u>Page</u>
EXECUTIVE SUMMARY	iii
1. INTRODUCTION	1
1.1 Background	1
1.2 Definition and Concepts of Durability and Service Life	2
1.3 Scope and Outline of Report	4
2. QUALITY OF CONCRETE	5
2.1 Concepts of Quality	6
2.2 Quality of Concrete	7
3. PERMEABILITY OF CONCRETE	8
3.1 Effect of Porosity on Permeability	8
3.2 Controlling the Permeability of Concrete	14
4. SULFATE ATTACK	18
4.1 Mechanism	20
4.2 Resistance of Concrete to Sulfate Attack	22
4.3 Models and Service Life Predictions	24
5. CORROSION OF STEEL REINFORCEMENT IN CONCRETE	29
5.1 Mechanism	30
5.2 Resistance of Reinforced Concrete	33
5.2.1 Environment	33
5.2.2 Reinforcing Steel	34
5.2.3 Alkalinity of Pore Solution	35
5.2.3.1 Effect of pH on Corrosion Threshold	35
5.2.3.2 Pozzolans	35
5.2.3.3 Carbonation	36
5.2.4 Domestic Chloride Ions	37
5.2.5 Concrete Cover and Quality	38
5.2.6 Stray Currents	40
5.3 Models and Service Life Predictions	40
5.3.1 Model by Tuutti	40
5.3.2 Model for Corrosion by Sea Water	46
5.3.3 Empirical Model	47
6. ALKALI-AGGREGATE REACTIONS	48

Table of Contents (Continued)

	<u>Page</u>
6.1 Alkali-Aggregate Reaction	50
6.1.1 Mechanism	50
6.1.2 Determination of Aggregate Reactivity	52
6.1.2.1 Petrographic Examination	53
6.1.2.2 Mortar-Bar Test for Potential Reactivity	53
6.1.2.3 Chemical Test for Potential Reactivity .	54
6.1.2.4 Combination of the Methods	54
6.1.3 Prevention of Alkali-Aggregate Expansive Reactions	55
6.2 Alkali-Carbonate Reaction	57
6.2.1 Mechanism	57
6.2.2 Determination of Potential Reactivity of Aggregates	58
6.2.3 Prevention of Alkali-Carbonate Reaction	58
6.3 Models and Service Life Predictions	59
7. FREEZING AND THAWING	61
7.1 Mechanisms	62
7.1.1 Hardened Cement Paste	62
7.1.2 Freezing in Aggregates	65
7.2 Factors Controlling Resistance to Frost Damage	65
7.2.1 Exposure to Moisture	66
7.2.2 Water-Cement Ratio	66
7.2.3 Entrained Air	66
7.2.4 Materials and Tests	68
7.2.5 Curing	71
7.3 Models and Service Life Predictions	71
7.3.1 Service Life Prediction Model	71
7.3.2 Model of Frost Penetration	73
7.3.3 Modeling of Freezing and Thawing Processes ..	73
8. DETERIORATION OF CONCRETE BY LEACHING	74
8.1 Mechanism	75
8.2 Factors Influencing Leaching	76

Table of Contents (Continued)

	<u>Page</u>
8.2.1 Permeability of Concrete	76
8.2.2 Underground Water Movement	77
8.2.3 Chemistry of Underground Water	77
8.2.4 Chemistry of Hydrated Cement Paste	79
8.3 Models and Service Life Predictions	79
9. OTHER DETERIORATION PROCESSES	83
9.1 Microbiological Attack	83
9.2 Salt Crystallization	86
9.3 Attack by LLW	87
10. EMPIRICAL KINETIC MODELS	88
11. RECOMMENDED RESEARCH PROGRAMS	90
11.1 Candidate Concretes	93
11.2 Recommended Approach for Predicting Service Lives ..	95
11.2.1 Accelerated Testing	100
11.2.2 In-Service Concrete Studies	102
11.2.3 Models for Service Life Prediction	103
11.3 Research Priorities	107
12. SUMMARY and CONCLUSIONS	109
13. ACKNOWLEDGMENTS	111
14. REFERENCES	112
APPENDIX A. Barrier Systems for Protecting Concrete Surfaces	A-1
APPENDIX B. Some Common Chemicals and Substances Aggressive to Portland Cement Concrete	B-1

LIST OF FIGURES

	<u>Page</u>
Figure 1. QA/QC activities in concrete construction	9
Figure 2. Effect of capillary porosity in hardened cement paste on permeability (9)	12
Figure 3. Effect of water-to-cement (w/c) ratio on permeability of concrete (14)	13
Figure 4. Effect of water-to-cement (w/c) ratio on permeability of hardened cement paste (19)	16
Figure 5. Major causes of cracks in concrete (22)	19
Figure 6. Schematic of corrosion of steel reinforcement in concrete	31
Figure 7. Effect of water-to-cement ratio and depth of concrete cover reinforcement on chloride ion penetration (38)	39
Figure 8. Schematic of conceptual model of corrosion of steel reinforcement in concrete (37)	41
Figure 9. Calculated induction period. Effects of concrete cover, threshold concentration, threshold concentration of chloride ions, concentration of chloride ions, and concrete permeability on calculated induction period (37)	44
Figure 10. Estimated fraction of calcium released per year from concrete by groundwater (89)	84
Figure 11. Estimated time dependence of pH within concrete exposed to groundwater (89)	85
Figure 12. Typical rates of deterioration. Meanings of t's are given in table 5	92
Figure 13. Methodology for developing and using accelerated tests in predicting service lives (5)	97
Figure 14. Schematic of proposed conceptual model of sulfate attack, by ettringite formation, of concrete	104
Figure 15. Method for predicting the advance of threshold concentration of aggressive solution concrete at in-service stresses, S_o , based on elevated stresses, S_m	106

LIST OF TABLES

	<u>Page</u>
Table 1. Classification of Pore Sizes in Hydrated Cement Pastes (13)	11
Table 2. Recommendations for Sulfate Resistance (23)	25
Table 3. Recommended Air Contents for Frost-Resistant Concrete (23)	69
Table 4. Composition of Some Natural Groundwaters (95)	87
Table 5. Durability of Models (98)	91

1. INTRODUCTION

1.1 Background

The U.S. Nuclear Regulatory Commission has the responsibility for developing a strategy for storing low-level radioactive wastes (LLW). According to one approach, the radioactive wastes would be stored in concrete vaults which are either buried in the earth or constructed above ground and covered with earth. A service life of 500 years is required for the storage vaults as they may be left unattended for much of their lives.

Several observations suggest that certain concretes could meet the 500 year requirement. For example, some concretes placed during The Roman Age are still intact (1). These concretes, however, may not be representative of the typical concrete of their era and statistically be only a minute sample of the population (e.g., one concrete structure out of a thousand or so surviving). Further, ancient concretes contain cements of significantly different composition compared to modern cements. Regarding the durability of modern concrete, there are some structures, with concretes based on portland cement, which have been in service for over one hundred years (2). Based on analysis of the permeability of concrete, Atkinson (3) has predicted that a high quality concrete could have a service life greatly exceeding 500 years if the exposure conditions are not severe. Therefore, based on consideration of the past durabilities of concrete, it appears possible to design concrete

to give service lives of at least 500 years in favorable environments.

The present basis for selecting concretes and their constituents needs to be further advanced to ensure that concretes with expected service lives of at least 500 years are designed. At least two approaches can be followed. In the first, the most durable concrete feasible could be developed and assumed that it will have the desired life. The other approach involves the development of performance criteria based on considerations of the factors controlling the service life of concrete. In the latter approach the results of accelerated durability tests could be coupled with the development and application of mathematical models to form a basis for predicting service lives of concrete. This approach has been described by Pommersheim and Clifton (4).

1.2 Definition and Concepts of Durability and Service Life.

Durability and service life are often erroneously interchanged. The distinction between the two terms is evident when their definitions as given in ASTM E 632 (5) are compared:

durability, the capability of maintaining the serviceability of a product, component, assembly or construction over a specified time. Serviceability is viewed as the capability of the above to perform the function(s) for which they are designed and constructed.

service life (of building component or material), the period of time after installation during which all properties exceed the minimum acceptable values when routinely maintained.

Both durability and service life incorporate the concept of design requirements being met or exceeded for a given time. They can be used as a basis for measuring the adequacy of durability analysis procedures. Frohnsdorff, et al., (6) suggest the following procedures:

- 1) Make a quantitative assessment of time to failure of a component or material when it is exposed to the expected in-service conditions. This estimate can be derived from either in-service performance tests or from accelerated aging tests.
- 2) Obtain test results which correlate with in-service performance.
- 3) Identify the degradation mechanisms causing failures at high and low stresses.

ASTM E 632 defines accelerated aging tests as ones in which the degradation of building materials is intentionally accelerated over that expected in-service. This is done in anticipation that the effects of in service stress levels can be predicted from performance at accelerated stress levels. Proper identification of degradation mechanisms is important in extrapolating test results obtained from accelerated aging to normal in-service

conditions. In the accelerated testing approach it is essential that the degradation process at accelerated stress levels is the same as that occurring under the expected service conditions.

1.3 Scope and Outline of Report

This report examines the basis for making service life predictions based on accelerated testing and mathematical modeling of factors controlling the durability of concrete buried in the ground. Deterioration processes are analyzed based on considerations of their occurrence, extent of potential destruction, and mechanisms. Approaches for preventing their occurrence are also discussed.

Two of the important factors controlling the service life of concrete are its quality and permeability as discussed in Sections 2 and 3. The performance of reinforced concrete subjected to sulfate attack, corrosive environments, alkali-aggregate reactions, freezing and thawing conditions, and leaching by water are covered in Sections 4 through 8. Some other possible deterioration processes are briefly covered in Section 9. Several proposed empirically based kinetic models are presented in Section 10 for major deterioration processes of concrete. A recommended research plan for developing methods for predicting the service life of concrete is presented in Section 11. This plan is ambitious and research priorities, therefore, are included. The performance of coatings and joint materials

for concrete are outside the scope of deterioration of concrete materials and, therefore, they are placed in Appendix A. Lists of inorganic and organic chemicals and substances which are known to attack concrete are presented in Appendix B.

The leaching of concrete by groundwater is also covered. It is recognized that NRC has stipulated that concrete vaults for underground storage of LLW are to be located above the groundwater table. However, in some 500 years the groundwater table could fluctuate. Also, precipitation which is lime-deficient, or which becomes acidic during percolation through soil, can be aggressive to concrete.

2. QUALITY OF CONCRETE

The performance of a concrete structure is usually no better than the quality of its materials and construction practices. The need for quality concrete increases directly with the severity of requirements placed on its performance. Clearly, the requirement that concrete to be used to construct storage vaults for LLW must be durable for 500 years, is a severe demand necessitating that close attention is given to the factors controlling its quality. Throughout this report the need for quality concrete is stated. Therefore, some concepts of quality and factors affecting quality of concrete are briefly discussed.

2.1 Concepts of Quality

Quality of concrete can be broadly defined as the totality of features and characteristics of concrete that bear on its ability to satisfy an established requirement. A working definition of quality often used is "fitness for use" (7). The level of quality is dependent on proper quality assurance and quality control practices. These terms have been defined by the Business Roundtable (8) as:

"Quality Assurance (QA) - a planned and systematic pattern of all actions necessary to provide adequate confidence that a product will conform to established requirements."

"Quality Control (QC) - implements the quality plan by those actions necessary for conformance to established requirements."

This is the definition of QC in a narrow sense. In a broader sense, QC involves quality of conformance plus control of the quality of design and evaluation of customer satisfaction (quality plan). Based on this broader scope, QC of concrete LLW vaults includes the control of quality by testing of physical and chemical properties of concrete materials and of fresh and hardened concrete, inspection of construction processes and practices, and evaluation of owner satisfaction.

Another aspect of an effective QA/QC program is quality audit. Quality audit is the determination of the conformance to established requirements. For example, testing of a LLW storage vault, and its components and concrete, when it is accepted by the owner, constitutes a quality audit.

2.2 Quality of Concrete

Many QA/QC activities and construction practices affect the quality of in-place concrete as indicated in Fig. 1. These QA/QC activities include checking the criteria for selecting concrete materials and for designing concrete, establishing requirements for quality, inspecting construction practices, testing of quality, and quality auditing of completed structure. The criteria for selecting materials and designing concrete should include performance and service life criteria. Once performance requirements are established in the preliminary design, ensuring that the materials meet the performance requirements is also a QC function. Construction practices which need inspection include the proportioning of concrete at the ready-mix plant, mixing of the constituents, placing and compaction of concrete, and curing of concrete. It cannot be overemphasized that good construction practices must be strictly followed in order to achieve concrete with a service life of 500 years.

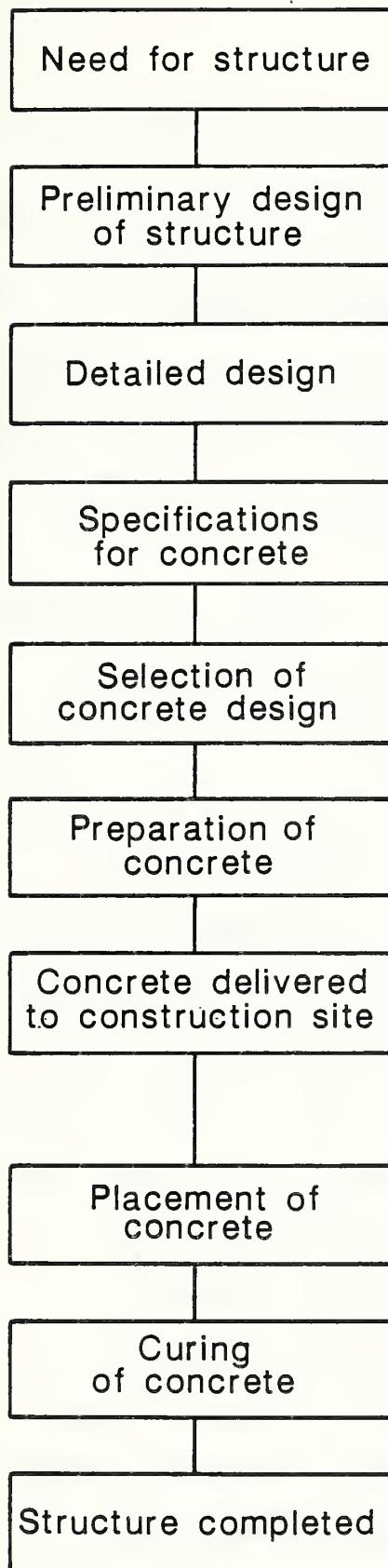
3 PERMEABILITY OF CONCRETE

3.1 Effect of Porosity on Permeability

Hardened concrete consists predominantly of mineral aggregates and hardened cement paste. A considerable amount of void space is distributed within the constituents of hardened concrete and also in regions between the constituents. However, most of the void space is located in the hardened cement paste. In cement technology, pore space in the hardened cement paste can be categorized into the following sequence of decreasing size ranges (table 1) : entrained air, capillaries, and gel pores. The minimum porosity of a completely hydrated cement paste is around 28 percent (9). Permeability of portland cement paste increases with porosity (Fig. 2) and with the extent that the pores are interconnected.

The water to cement ratio (usually expressed as the w/c ratio) of concrete is the most important factor in controlling the porosity of the hydrated cement paste and thus the permeability of properly prepared concrete. As the w/c ratio is decreased the porosity and consequently the permeability of concrete is decreased (Fig. 3). Permeability is an indicator of the ease of passage of liquids and gases in concrete. The permeability coefficient of a liquid flowing through a porous solid can be expressed by the following form of the D'Arcy equation (10):

$$Q = -kA/\mu (dP/dx) \quad (1)$$



- QA/QC planning
- Functional requirements for concrete
- Performance criteria for concrete
- Concrete proportions
- Concrete constituents
- QC inspection of:
 - Ready-mix plant procedures
 - Mixing of concrete
- QC tests:
 - w/c ratio (slump)
 - Air content
 - Density
 - Specimens taken for 28-day strength measurements
- Inspection of:
 - Consolidation
 - Finishing of concrete surface
- Proper curing depends on:
 - Temperature
 - Relative humidity
 - Wind
- Quality audit performed on concrete

Figure 1. QA/QC activities in concrete construction.

where Q is the volumetric flow rate (m^3/s), A is the cross sectional area (m^2) (for one-dimensional flow in the x direction), and μ is the viscosity of liquid ($\text{Pa}\cdot\text{s}$). P is the component of pressure capable of causing flow; k is the permeability coefficient which is a characteristic of the porous medium and independent of the fluid, provided that the fluid flow is viscous.

When considering water flow in concrete it is common to calculate the hydraulic conductivity, K , as given by the equation (10):

$$Q = AK(dh/dx) \quad (2)$$

where dh/dx is the hydraulic gradient across a specimen and is dimensionless. The hydraulic conductivity, K , is often referred to as the permeability and has the units of m/s . The permeability of hardened cement paste is around $10^{-16} \text{ m}/\text{s}$ for a w/c of 0.51, while the permeability for a hardened cement paste in which all capillary porosity has been eliminated is thought to be less than $10^{-22} \text{ m}/\text{s}$. Nyame and Illston reported (11,12) that the total porosity of hardened cement paste is not uniquely related to permeability, whereas the maximum continuous pore radius is uniquely related to permeability. The maximum continuous pore radius is representative of the size of pores in which the water flows. Depending on its w/c ratio, aggregate contents, and curing conditions the permeability of mature concrete (concrete

ble 1. Classification of Pore Sizes in Hydrated Cement Pastes (13)

signation	Diameter	Description	Role of Water	Paste Properties Affected
trapped Air	0.1-1.0mm	Round cross-section		Strength
pillary pores	10-0.05 um (50nm)	Large capillaries	Behaves as bulk water	Strength; permeability
	50-10nm	Medium capillaries	Moderate surface tension forces generated	Strength; permeability shrinkage at high humidities
1 Pores	10-2.5nm	Small (gel) capillaries	Strong surface tension forces generated	Shrinkage to 50% RH
	2.5-0.5nm	Micropores	Strongly absorbed water; menisci form	Shrinkage; creep
	< -0.5 nm	Micropores "interlayer"	Structural water involved in bonding	Shrinkage; creep

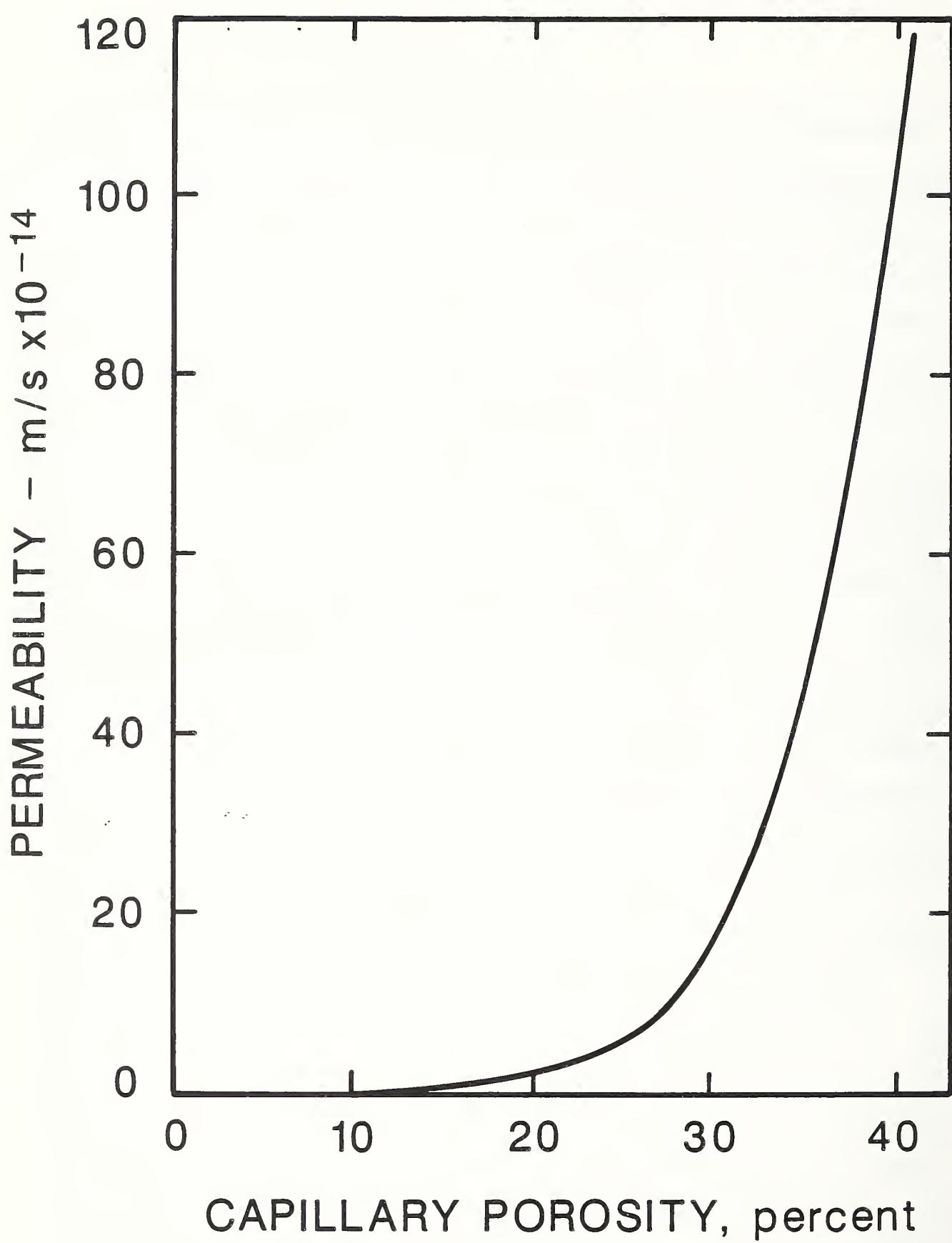


Figure 2. Effect of capillary porosity in hardened cement paste on permeability (9).

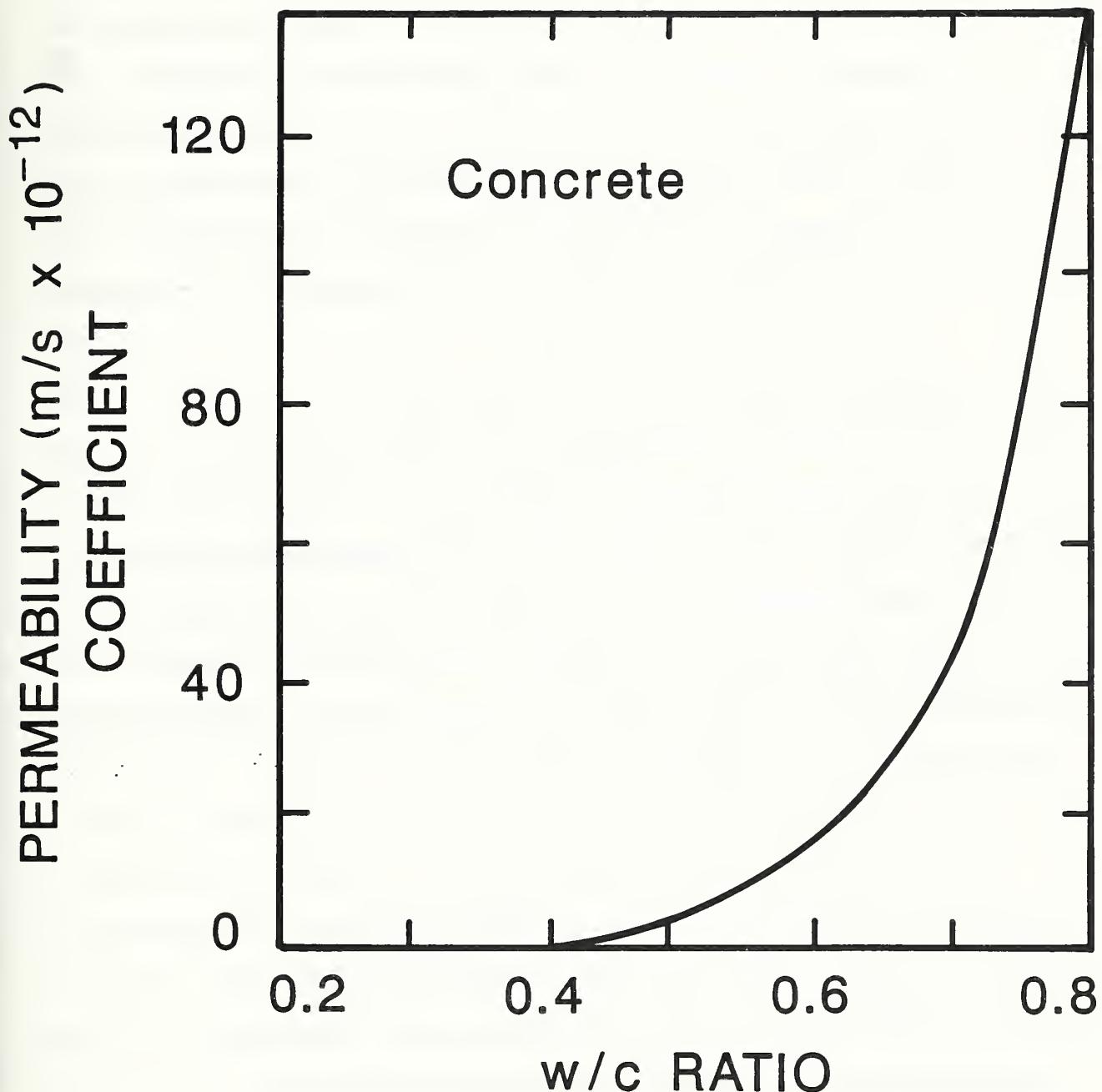


Figure 3. Effect of water-to-cement (w/c) ratio on permeability of concrete (14).

in which cement hydration is essentially complete) can range from 10^{-10} to 10^{-15} m/s (13). The permeability of concrete is higher than cement paste at the same w/c ratio for several reasons, including the development of microcracks at the cement-aggregate interface and of a low density transition zone in the cement matrix near the interface, segregation of particles creating bleeding channels, and lack of proper consolidation.

3.2 Controlling the Permeability of Concrete

Permeability of hardened cement paste can be reduced by decreasing the porosity, maximum size of pores, and by reducing the extent of inter-connectedness of pores. As illustrated in Fig. 4 (13), reducing the w/c ratio is an effective means of decreasing the permeability of hardened cement paste. However, significant decreases in the w/c ratio can result in difficulties with the placing and consolidation of concrete. These difficulties can be overcome by the use of water reducers. Normal water-reducing admixtures can reduce the w/c by around 15% (15). If a significant reduction in w/c is desired (between 20 to 33% for normal concrete (15)), then high-range water-reducing admixtures (HRWRA) can be used. HRWRA are also known as superplasticizers. In addition to making concrete more "flowable," HRWRAs can reduce the amount of bleeding. At a given w/c ratio, HRWRAs do not appear to affect the pore size distribution (16).

Another approach for reducing the permeability of concrete is to add pozzolanic materials which react with the $\text{Ca}(\text{OH})_2$ produced by the hydration of portland cement. This reaction produces more calcium silicate hydrate. Silica fume is a particularly reactive pozzolanic material because of its small particle (average particle diameter of around $0.1 \mu\text{m}$, which is about $1/100$ of the diameter of cement particles) and its high glassy silica content (between 85 to 98 percent). Studies by Sellevold, et al., (17) and by Cheng-yl and Feldman (18) indicate that silica fume does not significantly influence total porosity. It reduces the volume of capillary pores, while increasing the gel porosity, and significantly decreasing the volume of inter-connected pores. By producing smaller and more discontinuous pores, the addition of silica fume to concrete markedly decreases the permeability of concrete (16). Other pozzolans, which usually have finenesses comparable to cement, do not demonstrate this fine pore effect.

Because of the high surface area of silica fume, the water requirement for a flowable concrete is increased by silica fume addition. The need for more water can be compensated for by the addition of a HRWRA. The combination of HRWRA and silica fumes have been used to produce concretes with w/c ratios of 0.24 and lower, and compressive strengths greater than 127 MPa (18,400 psi) (20). Some uncertainty exists regarding the freeze-thaw durability of such concretes if entrained air is not present.

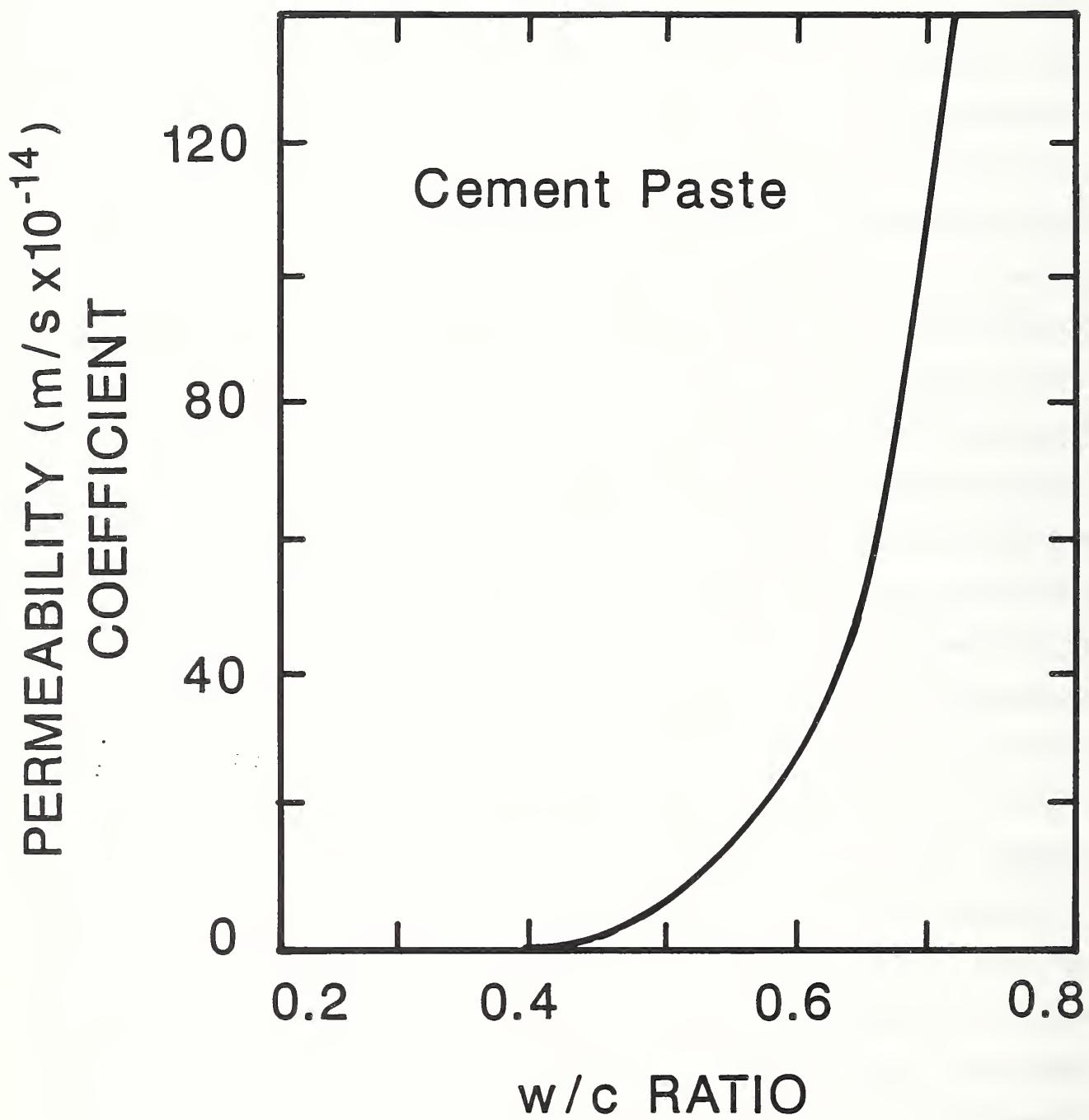


Figure 4. Effect of water-to-cement (w/c) ratio on permeability of hardened cement paste (19).

In addition to compositional and microstructural effects, other factors can have a significant effect on permeability. Browne and Domone (21) reviewed the permeability of concretes used in the construction of submersible structures. They concluded that, while permeability was a function of w/c ratio, aggregate content, and curing conditions, the main variable influencing permeability of concrete was the care with which it was placed. Another factor which could significantly influence the permeability of concrete is the occurrence of cracks. For example, in hard crystalline rocks, the flow of water is predominantly through long fissures, and, therefore, field permeabilities can be much greater than permeabilities measured in the laboratory on uncracked specimens. Alexander (10) showed that for viscous flow in stone fissures of width b with average spacing of s , the equivalent permeability (k_f) is given by;

$$k_f = b^3/12s. \quad (3)$$

Presuming that this equation is valid for concrete, then cracks with widths of 1 mm, spaced 1 m apart, would give an equivalent permeability of $8 \times 10^{-11} \text{ m}^2$ compared to an intact permeability of around 10^{-16} m^2 . The major types of cracks in concrete can be divided into those occurring before hardening and those occurring after hardening (Fig. 5). Those occurring before hardening can be caused by construction movement, plastic shrinkage or drying shrinkage, and early frost damage. The cracks occurring after

concrete has hardened involve physical, chemical, thermal and structural processes. Cracks occurring before hardening and most, if not all, of those occurring after hardening (especially those caused by design loads, drying shrinkage, crazing, and early thermal contraction) could be prevented by a proper QA/QC program.

4. SULFATE ATTACK

Probably the most widespread and common attack of concrete in contact with soil involves sulfates. Sulfate attack of concrete can be very deleterious resulting in cracking of concrete and in severe cases its disintegration. Naturally-occurring sulfates of sodium, potassium, calcium, and magnesium are sometimes found in groundwaters and soils, especially when high amounts of clay are present. If the sulfates are in groundwater and concrete is subjected to wetting and drying cycles by the groundwater, then upon evaporation of the groundwater from concrete surfaces the deposited sulfates may accumulate in the concrete at a concentration higher than that in the groundwater. Such processes can significantly accelerate sulfate attack, or also the attack by other aggressive salts such as chlorides. Sulfate attack has occurred in several regions of the United States, and is a particular problem in arid regions, such as the Northern Plains area and in the southwestern states (23). Localized sources of sulfates in groundwater include mine tailings, fills of blast-furnace slag, and deposits of chemical wastes.

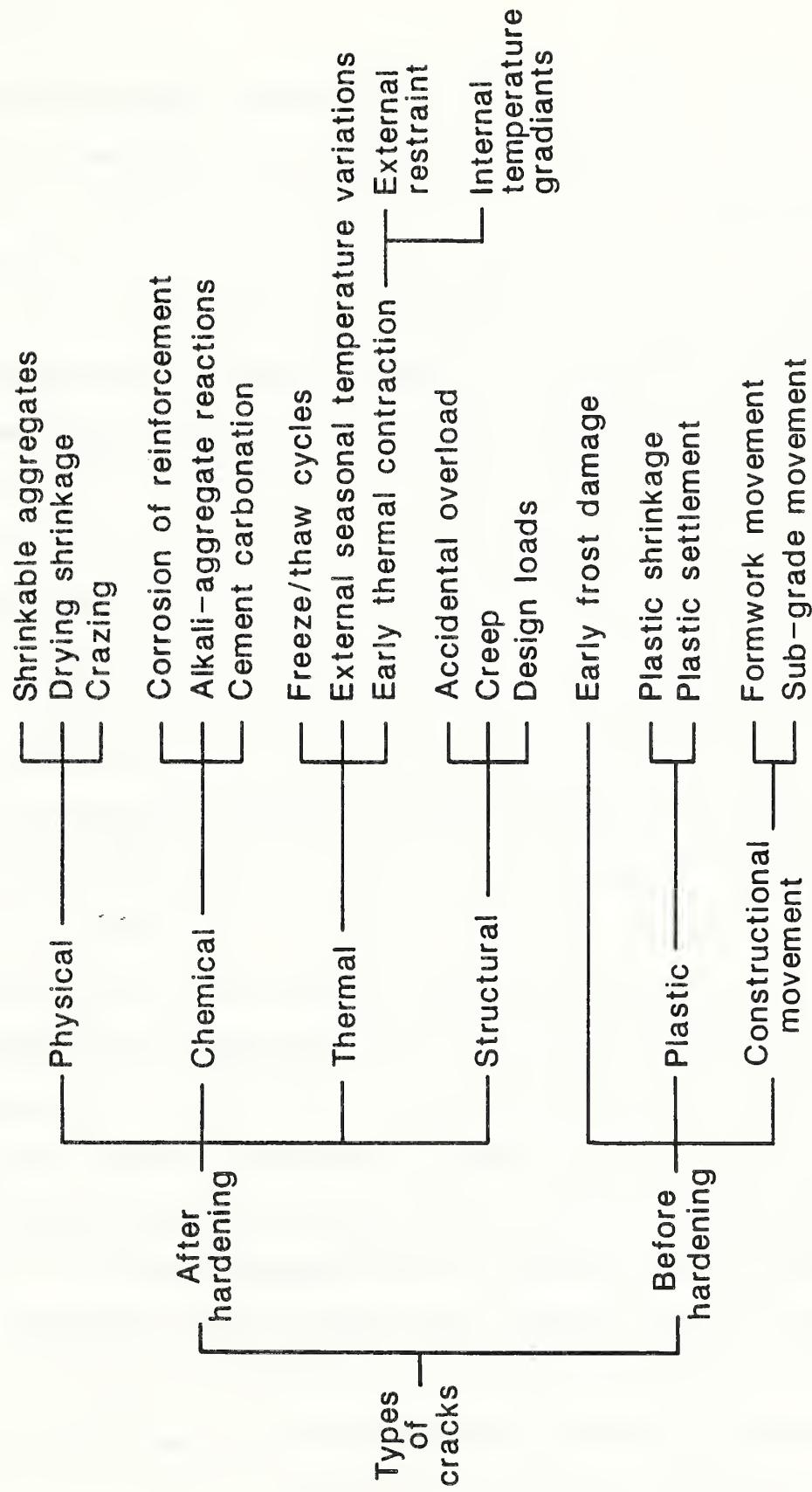


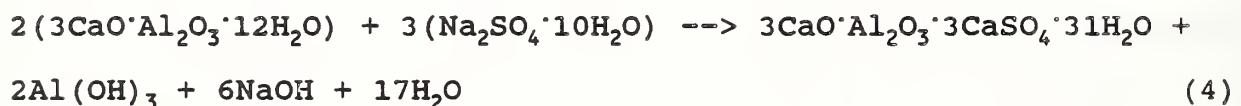
Figure 5. Major causes of cracks in concrete (22).

The water used in irrigation can be a potential source of sulfate attack because of the gradual accumulation of sulfates as the water evaporates.

4.1 Mechanisms

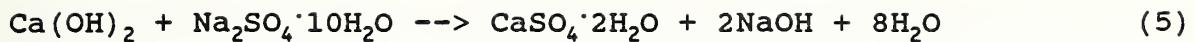
Sulfate attack of concrete is a complex process and at least three major deleterious reactions can take place depending on the environment (24,25).

The first process considered involves the reaction of sulfate ions with calcium aluminate hydrate to form the calcium sulfoaluminate product, ettringite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot31\text{H}_2\text{O}$):



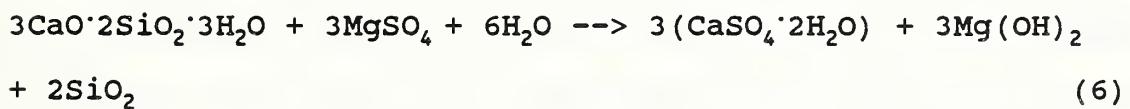
Ettringite has a considerably larger volume than the reactants. At low concentrations of sulfate ions, ettringite decomposes to a low sulfate form $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot12\text{H}_2\text{O}$. The amount of ettringite accumulated and the stress induced, therefore, depends on the availability of sulfate ions. The formation of ettringite appears to be the cause of most of the expansion and deterioration of concrete caused by sulfate solutions (23).

Another process involves the replacement of calcium hydroxide ($\text{Ca}(\text{OH})_2$) in concrete by gypsum ($\text{CaSO}_4\cdot2\text{H}_2\text{O}$):



Formation of gypsum can lead to the deterioration of concrete by two processes (25). In one process, because gypsum occupies more volume than calcium hydroxide, expansive stresses are produced. In another, gypsum is gradually leached, leaving a porous concrete with a higher permeability. In flowing water and given sufficient time, calcium hydroxide may be essentially completely converted to gypsum; while, in quasi-stagnant water, equilibrium will be attained and only a portion of the calcium hydroxide will be converted.

Similar reactions can occur involving magnesium sulfate. In addition, magnesium sulfate can attack the calcium silicate hydrate ($3\text{CaO} \cdot 2\text{SiO}_2 \cdot n\text{H}_2\text{O}$) formed by the hydration of portland cement. The reaction is of the pattern (25):



This reaction has particularly severe effects. Because of the very low solubility of magnesium hydroxide, the equilibrium is almost completely to the right. The reaction, however, is slow and is of greatest concern when concrete is exposed to sea water.

4.2 Resistance of Concrete to Sulfate Attack

Extensive research has been carried out on the resistance of concretes to sulfate attack. For example, Miller and Manson (26) carried out a 25-year investigation of the sulfate resistance of concrete using more than 75,000 specimens made from 122 commercial cements. Also, the Portland Cement Association (27) has been carrying out a comprehensive study of the resistance of concretes to sulfate-containing soils. The results of these and numerous other studies have clearly indicated that the tricalcium aluminate content of portland cement greatly affected its sulfate resistance (9, 23, 28). Accordingly, ASTM C 150 includes a Type V (sulfate resistant) cement which sets a maximum of 5%, by mass, on C_3A and a Type II (moderately sulfate-resisting) for which the C_3A is limited to 8%. There is also evidence that the aluminoferrite (C_4AF) phase of portland cement may participate in delayed sulfate attack and, thus, limits have been placed on its contents. The traditional practice of relying on such cements for acceptable sulfate resistance is being replaced with the recent practice of using low-permeability, low $Ca(OH)_2$ containing concrete (28). The sulfate resistance of concrete can be increased either by adding pozzolans or granulated blast-furnace slag to the concrete, or by using blended cements containing a pozzolan or a granulated blast furnace slag. These mineral admixtures react with the $Ca(OH)_2$ produced by the cement hydration to produce additional calcium silicate hydrate which reduces the capillary porosity and thus permeability. Also,

decreasing the $\text{Ca}(\text{OH})_2$ contents will reduce the amount of concrete expansion caused by the formation of gypsum (equation 5). The US Bureau of Reclamation (29) carried out a 12 year study on the effect of the composition of fly ash on the sulfate durability of concrete. It was found that the effectiveness of a fly ash on improving the sulfate resistance of concrete could be predicted based on its CaO and Fe_2O_3 contents. Based on the ASTM C1012 test method, silica fume has been observed to improved the sulfate resistance of mortar bars (Hooten). Long-term durability tests on the sulfate resistance of concrete containing silica fume, however, have not been reported. The effectiveness of mineral admixtures in preventing sulfate attack depends on their composition and physical properties, and, therefore, they should conform to the appropriate ASTM standards before being used.

Recommendations for selecting cements and mineral admixtures for concretes exposed to sulfates have been given in the ACI Guide for Durable Concrete (23). The recommendations are presented in table 2. Also, they are presented in an expert system form in Durcon (30). Although ASTM Type V portland cement is recommended in the table for severe and very severe exposures, little Type V cement is available in the United States (31). In the case of a severe environment, a Type II portland cement with blast furnace slag or a pozzolan should be an adequate substitute for Type V.

A site with a very severe environment is, undoubtedly, unfit for storing LLW in concrete vaults. Following these recommendations should result in a concrete with acceptable durability for many years, possibly for the 60 to 100 year design life of typical concrete structure. However, they do not provide a basis for predicting the service life of a concrete exposed to a sulfate environment, especially in the case of concrete with a design life of hundreds of years.

4.3 Models and Service Life Predictions

Two major studies have been reported (32, 33) on approaches for estimating the service life of concrete exposed to sulfates. In the first, the US Bureau of Reclamation (32), continuously immersed concrete specimens in a 2.1% Na_2SO_4 (sodium sulfate) solution until failure (expansion of 0.5%) or until the investigation was completed. The age of specimens at the completion of the continuous-immersion study was between 18 to 24 years. Companion specimens were subjected to an accelerated test in which they were immersed for 16 hours in a 2.1% Na_2SO_4 solution and then forced air dried at 54°C (130°F) for 8 hours. From a comparison of the times for specimens to reach an expansion of 0.5% in both the accelerated test and the continuous immersion test, it was estimated that 1 year of accelerated testing equalled 8 years of continuous immersion. This was considered to be a conservative ratio as a 1:10 ratio was

Table 2. Recommendations for Sulfate Resistance (23)

Exposure	Water soluble sulfate (a) soil, percent	Soluble (SO ₄) in water, ppm	cement	Water-cement ratio, maximum(b)
Mild	0.00-0.10	0-150	---	---
Moderate (Includes Seawater)	0.10-0.20	150-1500	Type II IP (MS) IS (MS) (c)	0.50
Severe	0.20-2.00	1500-10,000	Type V (d)	0.45
Very Severe	Over 2.00	Over 10,000	Type V + Pozzolan or Slag (e)	0.45

(a) Sulfate expressed as SO₄ is related to sulfate expressed as SO₃ as in reports of chemical analysis of cement as SO₃ X 1.2 = SO₄.

(b) A lower water-cement ratio may be necessary to prevent corrosion of embedded steel.

(c) Or a blend of Type I cement and a ground granulated blast-furnace slag or pozzolan that has been determined by tests to give equivalent sulfate resistance.

(d) Or a blend of Type II cement and a ground granulated blast-furnace slag or a pozzolan that has been determined by tests to give equivalent sulfate resistance.

(e) Use a pozzolan or slag that has been determined by tests to improve sulfate resistance when used in concrete containing Type V cement.

thought to be more realistic. In many cases, the time for the concretes in the continuous immersion test to expand by 0.5% was estimated by straight-line extrapolation. They concluded that most of the concretes with Types II and V portland cements showed a life expectancy of less than 50 years when exposed to a 2.1% Na_2SO_4 solution. Some concretes containing certain fly ash and ground blast-furnace slag mineral admixtures had estimated service lives of 150 years or more. A 2.1% solution of Na_2SO_4 is a very severe environment (table 2) and if concrete was exposed to a lower level of sulfates the life expectancy would be expected to increase. In addition to providing an approach for service life estimates, the accelerated test results clearly demonstrate the aggressive effect of wetting and drying cycles with sulfate solutions on the durability of concrete.

The above method could be used for predicting the service lives of in-service concretes, in continuous contact with groundwater, if the ratio of 1:8 for the time to attain a equivalent expansion in the accelerated and continuous immersion tests using the 2.1% sulfate solution holds for other sulfate concentrations. Based on the ratio of 1:8, however, to predict if a concrete would have a life expectancy of 500 years may necessitate an unacceptably extended extrapolation of the accelerated test results as follows. Assuming that a concrete with a life of 500 years was actually being tested, then to predict that the concrete would have a life expectancy of 500 years by testing until the 0.5%

expansion criterion was reached in the accelerated test would require a testing period of at least 500/8 years, i.e., 63 years. Unfortunately, few durability tests are carried out for 63 years and a 5 to 10 year test is often considered long-termed. If the accelerated test was terminated in 5 years, the expansion for the 500-year-life concrete would be no more than 0.04% and little confidence could be given to predictions based on extrapolating the expansion data to 0.5%.

Another approach to predicting the service life of concrete exposed to groundwater containing sulfate salts was developed by the Building Research Establishment in England (33). In the laboratory, concrete specimens were immersed in a 0.19M sulfate solution (a mixture of alkali and magnesium sulfates) for up to 5 years. The accelerated laboratory tests resulted in a visible deterioration zone, x_s , and the following empirical equation was developed:

$$x_s(\text{cm}) = 0.55CA(\%) \cdot ([\text{Mg}] + [\text{SO}_4]) \cdot t(y) \quad (7)$$

where CA% is the percentage by weight of tricalcium aluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$) in the cement, $[\text{Mg}]$ and $[\text{SO}_4]$ are the molar concentrations of magnesium and sulfates, respectively, in the test solution, and $t(y)$ is the test time in years. The variability in the depths of attack were around 30% of the average.

Equation no. 7 was found to give satisfactory correlations with the results of field tests (3), in which the depth of penetrations were in the range of 0.8 to 2 cm after 5 years. The equation was used to calculate a range of lifetimes of concrete exposed to groundwater of a known concentration of sulfate salts. Concretes made with ordinary portland cements containing between 5 and 12% C_3A , gave estimated lifetimes of between 180 to 800 years, with a probable lifetime of 400 years. When a sulfate resisting portland cement with 1.2% C_3A was used, the minimum and probable lifetimes were estimated to be 700 years and 2500 years, respectively. These times were estimated based on the loss of one-half of the load-bearing capacity of a 1 m thick concrete section, i.e., X_s of 50 cm. The estimates involve an extrapolation based only on an empirical equation that has been shown to be reasonably predictive only during short-term testing. Atkinson, et al., (3) attempted to verify the equation by determining the extent of deterioration of concretes buried and exposed to the groundwater of a clay for 43 years. An alteration zone of about 1 cm was observed in the concretes which could be caused by several processes. Based on the tricalcium aluminate contents of the cements, equation no. 7 predicts that the thickness of the deteriorated region should be between 1 and 9 cm. Therefore, Atkinson, et al., (3) concluded that the equation either gives a correct estimate or an overestimate of the rate of sulfate attack.

5. CORROSION OF STEEL REINFORCEMENT IN CONCRETE

Portland cement concrete normally provides an internal environment which protects reinforcing steel from corrosion. The high alkaline environment ($\text{pH} > 12.5$) in concrete results in the formation of a tightly adhering film (gamma iron (III) oxide) which passivates the steel and thereby protects it from corrosion. However, the corrosion of steel embedded in concrete has become a serious problem in recent years in certain types of structures, e.g., bridges and parking garages. Chloride ions are considered to be the major cause of premature corrosion of steel reinforcement in many of these structures. Chloride ions are common in nature and small amounts are usually unintentionally contained in the mix ingredients of concrete. Chloride ions also may be intentionally added, most often as a constituent of accelerating admixtures. The sources of chloride ion which are causing the most problems, however, are deicing salts (usually calcium chloride) and sea water.

In addition to natural deposits of chloride salts, groundwater may be contaminated with chloride ions coming from runoff water, e.g., from bridges or pavements treated with deicing salts.

Corrosion can occur in some cases in the absence of chloride ions. For example, carbonation of concrete results in reduction of its alkalinity and, thereby, can depassivate the steel and initiate corrosion. Carbonation, however, is usually not a

problem with dense concrete and with a proper cover of concrete over the reinforcement. Corrosion also can occur in concrete through the formation of concentration cells (34,35).

Because of the predominant role that chloride ions plays in corrosion of reinforcing steel, their effects on the durability of concrete will be largely addressed herein. Also, protecting reinforced concrete from chloride ions should also improve its durability towards other corrosive substances.

5.1 Mechanism

The corrosion of steel in concrete is almost always electrochemical in nature. Its process is similar to the action occurring in a battery, involving the formation of cathodic and anodic poles, an electrical conductor (the reinforcing bar), and an aqueous electrolyte (the pore solution in concrete) (Fig 6). Reactions at the anodes and cathodes are usually referred to as "half cell reactions" (36). At the anode, iron is oxidized to iron(II) (ferrous) ions:



At the cathode, reduction takes place. In the alkaline environment of concrete the cathodic reaction is:



The overall (cell) reaction is:

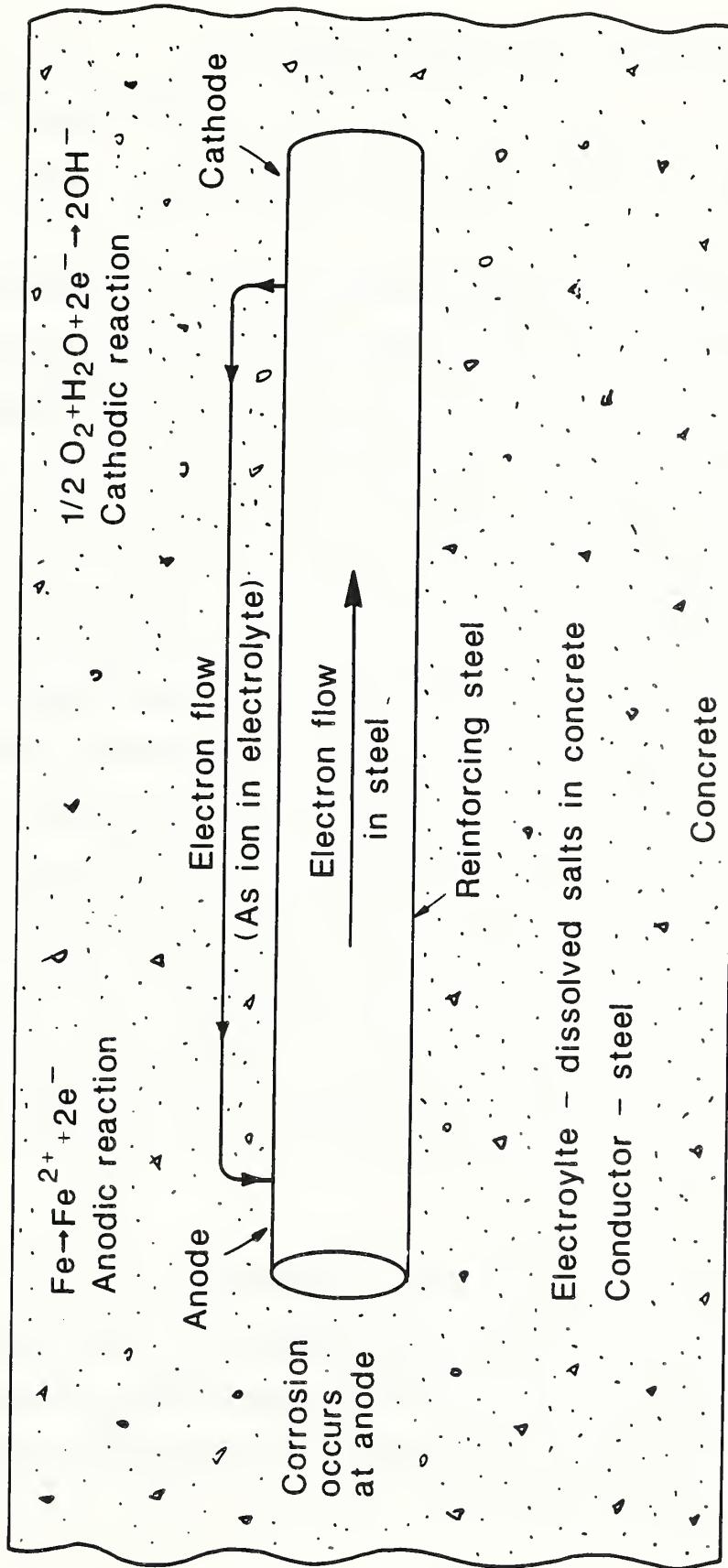


Figure 6. Schematic of corrosion of steel reinforcement in concrete.



Other subsequent reactions occur with Fe(OH)_3 being formed. It precipitates as $\text{FeO} \cdot \text{OH}$ which gives the characteristic rust color.

Equation (9) indicates that both water and oxygen must be present for the corrosion to occur. With only water and oxygen present, however, the reaction proceeds very slowly and with good quality concrete the resulting rate of corrosion may be very small under normal environmental conditions (37). Chlorides can accelerate the corrosion rate so that corrosion can be a serious problem within a few years. For example, bridge decks which are treated with chloride-ion-containing deicing salts have been known to deteriorate a few years after construction because of corrosion of reinforcing steel (36). The process by which chloride ions cause the accelerated corrosion of reinforcing steel is not unequivocally known, but chloride ions are thought to depassivate steel by dissolution of or by a physical breakup of the protective oxide layer on the steel (36). Chloride ions also can reduce the electrical resistance of concrete which can increase the corrosion current.

The corrosion products of reinforcing steel have a volume several times (36, 37) that of the original iron, which can result in the development of internal tensile stresses leading to the cracking of the concrete. If corrosion is allowed to proceed

unabated, it can ultimately result in the destruction of reinforced concrete.

5.2 Resistance of Reinforced Concrete.

The resistance of reinforced concrete to corrosion is dependent on several important factors including the environment, the permeability of the concrete, the concrete constituents, the depth of cover of concrete over the reinforcement, and the quality of the concrete.

5.2.1 Environment

It is anticipated that concrete vaults buried in soils will not be exposed to seawater nor will deicing salts be directly applied to them. However if such severe environments are encountered, the use of special protective measures must be considered including the use of coatings or sealers for concrete, dense concrete overlays, metallic and organic coatings for reinforcing steel, corrosion inhibitors, and cathodic protection. These practices are described in the report prepared by ACI Committee 222, Corrosion of Metals in Concrete (36).

The severity of the corrosive environment will be largely dependent on the soluble content of the soil and groundwater. Similar to the case with sulfate ions, wetting and drying cycles with aqueous solutions of chloride ions can result in the concentration of chloride ions deposited in the pores of the

concrete being much higher than the concentration in the groundwater.

By this process, the corrosion of reinforcing steel can be significantly accelerated. This is the basis for an accelerated corrosion test for reinforced concrete developed by the Federal Highway Administration (38).

5.2.2 Reinforcing Steel

In dealing with severe corrosive environments, changes in the metallurgy of reinforcing steel have been considered. However, the susceptibility to corrosion of typical reinforcing steel (mild steel) is not thought to be significantly affected by its composition, grade, or level of stress (39). Stainless steel reinforcement has been used in special applications, especially as hardware for attaching panels in precast concrete construction. Stainless steel, however, is too expensive as a replacement for typical reinforcing steel in most cases. Stainless-steel-clad bars have been found to reduce the frequency of corrosion-induced cracking compared to mild steel, but did not prevent it (36). Fusion-bonded epoxy powder coatings have been found to be effective in protecting steel reinforcement from corrosion (40) and they have been widely used in bridge decks.

5.2.3 Alkalinity of Pore Solution

5.2.3.1 Effect of pH on Corrosion Threshold

The chemistry of the pore solution in concrete was shown by Hausman (41) to influence the initiation of corrosion by chloride ions. In studies carried out in sodium hydroxide solutions and saturated calcium hydroxide solutions, he found evidence for a relationship existing between the chloride ion concentration necessary to induce corrosion (threshold concentration) and the activity of the hydroxide; with the threshold level significantly decreased as the pH is lowered. For example, at a pH of 13.2 more than 8000 ppm of chlorides ions were required to induce corrosion, while at a pH of 11.6 around 71 ppm of chloride ions were sufficient to induce corrosion.

5.2.3.2 Pozzolans

The effect of pH on the threshold concentration of chloride ions poses an interesting dilemma in deciding whether to use a pozzolan. Pozzolans react with the hydroxide ions resulting from the hydration of portland cement and thus can reduce the pH of the pore solution. Thus it would appear that the use of pozzolans would decrease the resistance of reinforced concrete to corrosion. The effect of pozzolans, however, on reducing the permeability of concrete has been reported (42) to more than compensate for the lowering of pH. Also, the amount of pozzolan added can be adjusted so that sufficient amounts of hydroxide ions remain to maintain a high pH. Concrete usually has a high

reserve basicity because most of the calcium hydroxide is not in solution which can be dissolved as a pozzolan reacts with the pore solution. While, it seems likely that concretes with pozzolans should adequately protect reinforcing steel from corrosion, this assumption has not been verified by long-term studies.

5.2.3.3 Carbonation

Carbonation of concrete by carbon dioxide reduces the pH of the pore solution in the affected regions. If the depth of carbonation extends to the reinforcing steel, then the chloride ion threshold concentration can be significantly reduced.

Carbonation follows the general equation (43):

$$\frac{dx}{dt} = Kt^{1/2}. \quad (11)$$

in which the proportionality constant K depends on several parameters relevant to the quality of concrete and to the environment.

The rate and extent of carbonation depends on the environmental relative humidity, reaching a maximum at 50% relative humidity (43). Diffusion of gaseous carbon dioxide takes place several orders of magnitude more rapidly through air than through water. If the pores of concrete are saturated with water, the amount of carbonation occurring will be negligible. In most cases, the time

needed to carbonate 2 cm of high-quality concrete is reported (44,45) to be of the order of tens of years, and the penetration rate of carbon dioxide rapidly falls well below a mm/year soon after construction. Carbonation can be a serious problem, however, if the reinforcing steel is closer to the concrete surface than recommended, e.g. in ACI 318 (46). High temperatures, such as those which occur in Middle East countries, appear to increase the severity of corrosion attributed to carbonation (43, 47, 48).

Another process by which the pH of concrete can be reduced is by the leaching of soluble alkaline salts with water, especially if the water contains high levels of dissolved carbon dioxide. This process is discussed in Section 9 on groundwater.

5.2.4 Domestic Chloride Ions

In some cases sufficient chloride ions have been present in the constituents (called "domestic" chloride ions (36)) of concrete to cause corrosion. For example, aggregates may have entrapped sea water during their formation which could be leached out by the concrete mix water. Also, certain chemical admixtures, especially set accelerators containing calcium chloride, can contain corrosive amounts of chloride ions. Recognizing that domestic chloride ions can induce corrosion, ACI Committee 222, Corrosion of Metals in Concrete, recommends (36) the following

maximum acid-soluble chloride ions, expressed as percent by mass of the cement, be permitted in reinforced concrete:

Prestressed concrete - 0.08%

Reinforced concrete - 0.20%

Domestic chloride ions have been found to be tied up by the tricalcium aluminate of portland cement to form calcium chloroaluminates (39). While using cements with high tricalcium aluminate contents may be of benefit in reducing corrosion problems, the potential for sulfate attack will be increased.

5.2.5 Concrete Cover and Quality

The results of numerous studies (37,38,39) have indicated that a proper concrete cover over the reinforcing steel is vital in preventing corrosion. Combination of a low w/c ratio and the recommended cover (e.g., as given in ACI 318 (46)) can significantly improve the resistance of reinforced concrete to corrosion caused by chloride ions. The effect of w/c ratio and the depth of concrete cover on the ingress of chloride ions is shown in Fig. 7.

Good concrete construction practices are necessary for obtaining corrosion-resistant reinforced concrete. Poor consolidation, excessive bleeding, and presence of honeycombing can result in non-uniform concrete with higher than anticipated permeability,

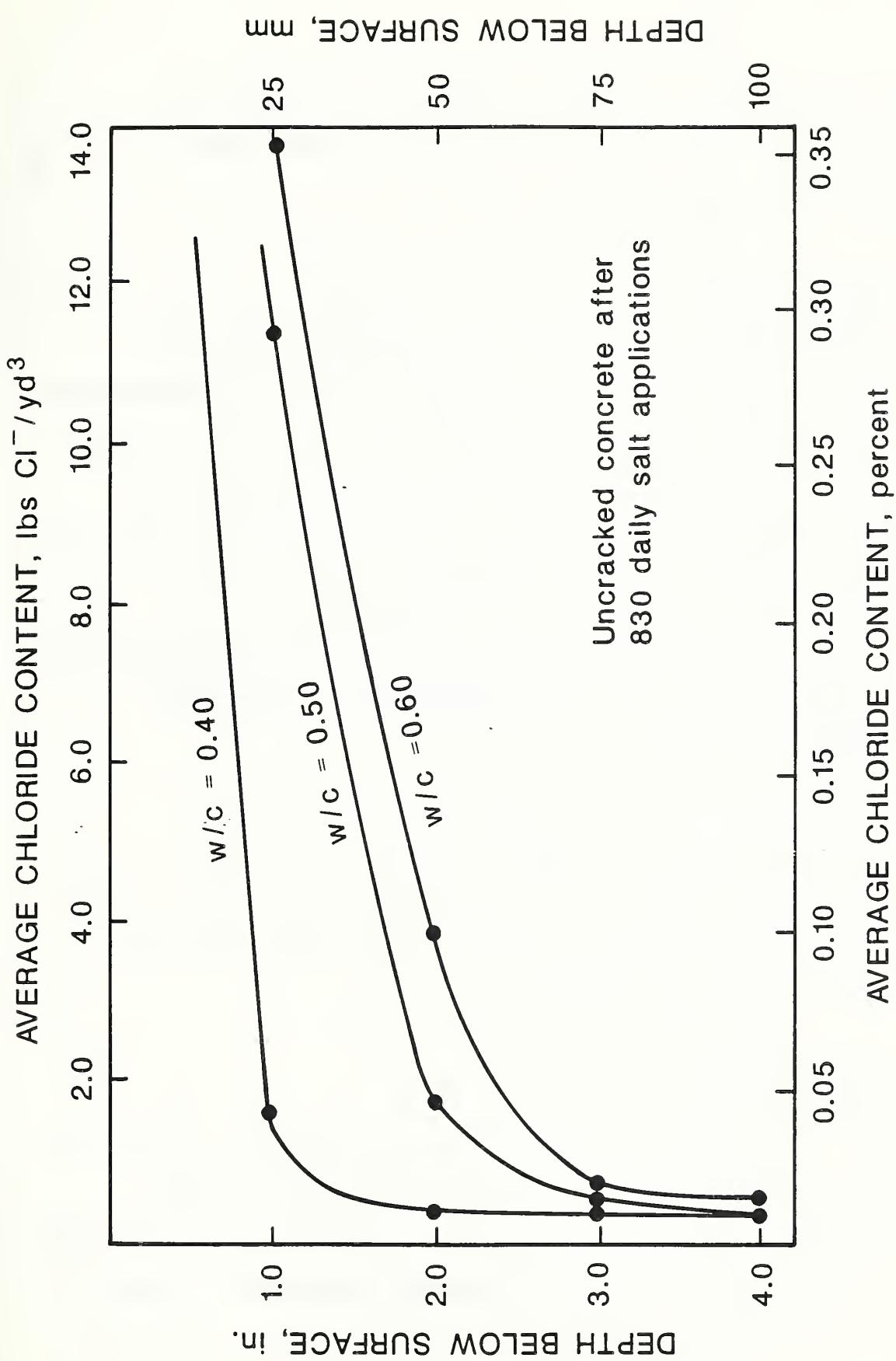


Figure 7. Effect of water-to-cement ratio and depth of concrete cover reinforcement on chloride ion penetration (38).

as well as resulting in the development of concentration corrosion cells. Also, proper curing is important for the attainment of low permeability.

5.2.6 Stray Currents.

Stray currents can be a potential problem with reinforced concrete structures buried in the ground. Stray currents can be defined as currents that follows paths other than the intended circuit (36). They can greatly accelerate the corrosion of reinforcing steel. The most common sources of stray currents are electrical railways, electroplating plants, and cathodic protection systems. Cathodic protection systems are often used to protect underground metal pipes transporting petroleum products and natural gas.

5.3 Models and Service Life Predictions.

Three models which can be used for predicting the service life of reinforced concrete exposed to chloride ions were disclosed during the course of the review.

5.3.1 Model by Tuutti

Tuutti (37) has developed a model for predicting the service life of reinforcing steel which will be outlined in some detail because it appears to provide a means for predicting the life of concrete structures buried in the ground. His model is based on the corrosion sequence schematically shown in Fig. 8. In this

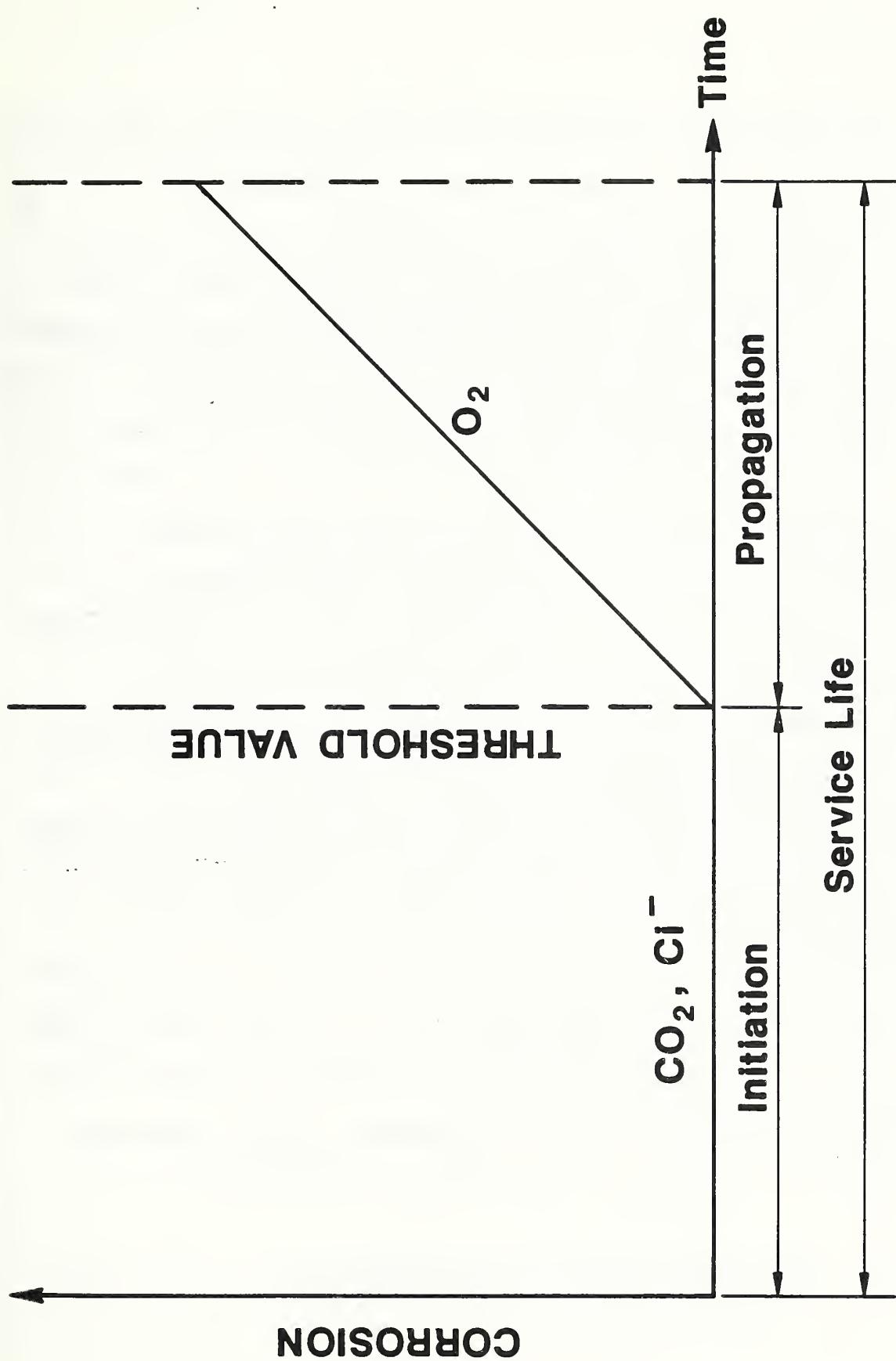


Figure 8. Schematic of conceptual model of corrosion of steel reinforcement in concrete (37).

model, corrosion starts after the end of an initiation period (dominant period of no corrosion) which is followed by a propagation period (period of active corrosion). The corrosion process is initiated by the diffusion of chloride ions to the depth of the reinforcing steel or by carbonation reducing the pH of the pore liquid in contact with the steel, or by the combination of chloride ions and carbonation.

In the following, only the effect of chloride ions on the initiation period will be considered. The length of the initiation period is largely controlled by the rate of diffusion of the chloride ions in the concrete and by the threshold concentration for the process. Because chloride ions may react with the tricalcium aluminate of portland cement the concentration has two components; concentration of bound chloride ions (c_b) and concentration of free ions (c_f), related by the constant R (37):

$$c_b = R \cdot c_f. \quad (12)$$

The diffusion equation (D), in one dimension, can be expressed as:

$$\frac{\partial c_{\text{free}}}{\partial t} = [D/(R + 1)] \cdot \frac{\partial^2 c_{\text{free}}}{\partial x^2} \quad (13)$$

where $D/(R + 1) = D_{\text{eff}}$, the effective diffusion coefficient, x is distance, and t is time.

In addition to the pH of the pore solution, the threshold concentration of chloride ions depends on the moisture content and the potential of the steel. The chloride ion threshold for water-saturated concrete should be in the range of 5,000 to 11,000 ppm. (49). The effects of concrete cover, threshold concentration of chloride ions, concentration of chloride ions, and concrete permeability on the calculated induction period are shown in Fig 9.

The corrosion rate in the propagation period is controlled by the rate of oxygen diffusion to the cathode, resistivity of the pore solution, and temperature. The diffusion resistance to oxygen is determined by the water saturation of the concrete cover and by the cross-section of pores not filled with water, which are dependent on the concrete's porosity, pore size distribution, inter-connectiveness of pores, and ambient relative humidity.

The combined mass transfer coefficient, K_t , is given by (37):

$$K_t = K_{\text{air}} + (K_{\text{H}_2\text{O}})/m \quad (14)$$

$$= (8 \cdot 10^{-7}/X_{\text{air}}) + 10^{-7}/4 \cdot 10^4 \cdot X_{\text{H}_2\text{O}}.$$

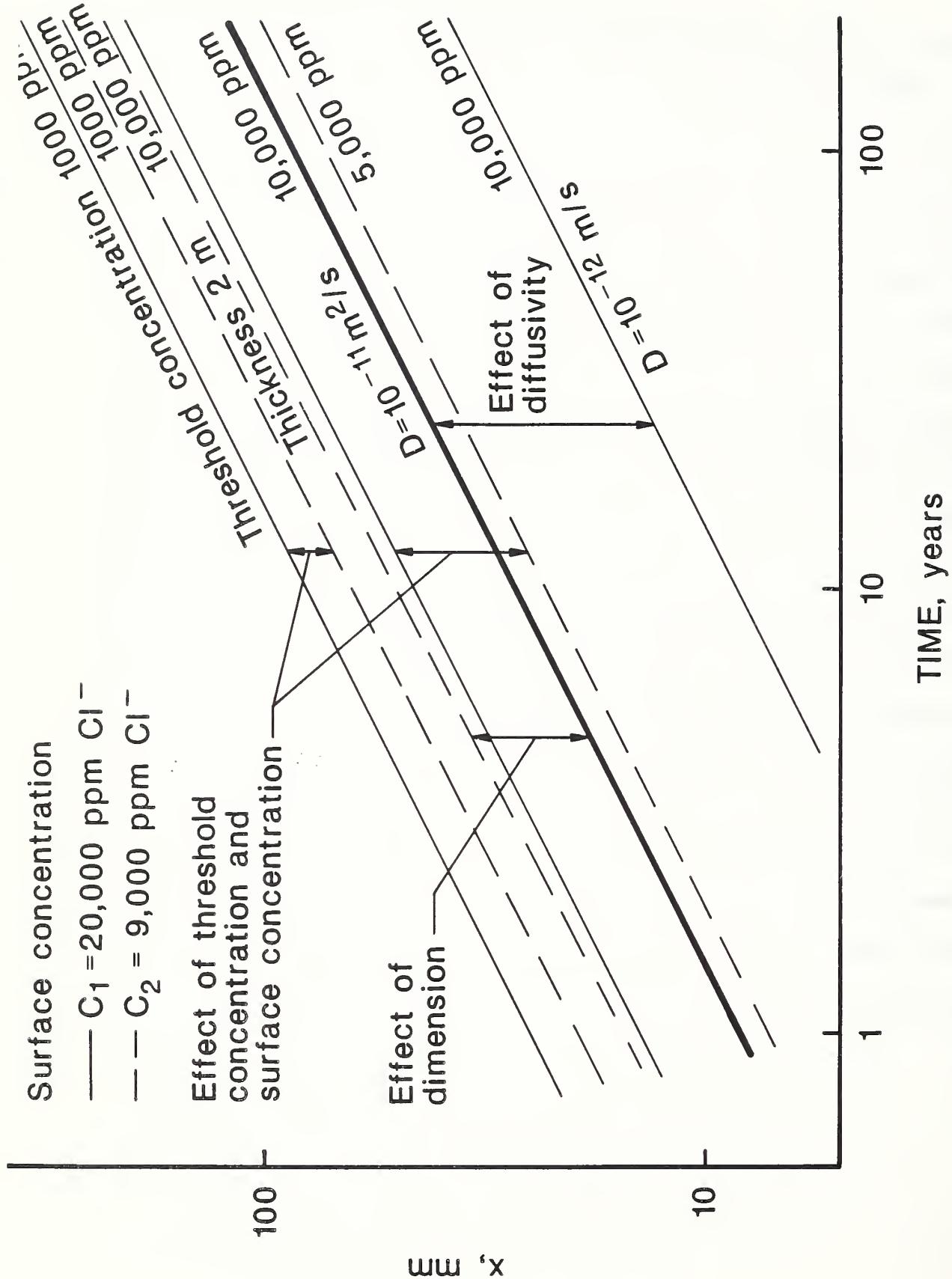


Figure 9. Calculated induction period. Effects of concrete cover, threshold concentration, threshold concentration of chloride ions, concentration of chloride ions, and concrete permeability on calculated induction period (37).

where m is a temperature dependent constant and X is the distance in either air or water filled pore or pore network. Clearly, the migration of oxygen through saturated concrete will be a substantially slower process than through partially water filled concrete and can become the rate controlling process. The effects of water in the pores on corrosion is demonstrated by the observation that corrosion at a relative humidity of 100% is negligible (50).

In using the model for predicting service lives, the recommended procedure by Tuutti (37) is given by the following steps:

Step 1. Compile the relevant material, structural, and environmental data.

Step 2. Calculate initiation time, based on experimental data for the diffusion rates and threshold concentration of corrosive substances.

Step 3. Calculate the corrosion rate in the propagation stage.

Step 4. Determine the amount of steel corrosion required to cause failure.

Tuutti (37) has provided values for many of the model parameter which can be used in estimating the service life of reinforced concrete exposed to corrosive environments. Also, he has given

recommendations on methods for obtaining values for the other parameters. The model appears to provide a means for making semi-quantitative predictions of the minimum service life of concrete structures.

5.3.2 Model for Corrosion by Sea Water

A model somewhat similar to that of Tuutti (37) was developed by Bazant (51) for corrosion of reinforced concrete exposed to sea water. This model is comprehensive and mathematically describes the following processes:

- (1) diffusion of oxygen and chloride ions in pore water,
- (2) diffusion of iron (II) hydroxide near steel surface,
- (3) depassivation of steel due to chloride ions,
- (4) effects of oxygen and iron (II) hydroxide on cathodic and anodic potentials and their polarizations,
- (5) flow of electrical current through the electrolyte in pores,
- (6) mass sinks for oxygen, iron (II) hydroxide, and hydrated red rust, and
- (7) rust production rates based on reaction kinetics.

The complete equation system is quite complicated and its complete solution has not been accomplished. Nevertheless, the model is based on a logical approach for developing, from theory, a method for calculating the service life of reinforced concrete. Based on some simplifying assumptions, the use of the model to

predict the service life of concrete structures in sea water has been demonstrated. For example, it predicts that a deeply submerged reinforced concrete structure could have a service life (considering only corrosion) of some 15,000 years (52). The model, perhaps, could be modified to address the case of reinforced concrete buried in soil. However, in the present form it is not obvious that this model has any advantages over that developed by Tuutti.

5.3.3 Empirical Model

Browne (53) developed an empirically based method for predicting the remaining service life of in-service reinforced concrete structures. The procedure for making predictions is:

(1) Samples are obtained from a concrete structure at different depths from the concrete surface and their chloride contents are determined.

(2) Use the equation

$$c(x,t) = c_0 [1 - \operatorname{erf}(x/2D_{cl} \cdot t)]^k \quad (15)$$

(where $c(x,t)$ is the chloride concentration at depth x after time t , for an equilibrium chloride concentration of c_0 at the surface; D_{cl} is the chloride ion diffusion coefficient; and erf

is the error function (obtained from standard statistical tables)), to obtain values of c_0 and D_{Cl} .

(3) Once the values of c_0 and D_{Cl} are obtained, then the chloride ion concentration at any distance from the surface can be calculated using equation no. 15.

(4) A chloride ion concentration of 0.4%, based on weight of cement, is used by Browne as the threshold value. The time to reach the threshold concentration at the depth of the reinforcing steel gives the remaining service life.

If the value of D_{Cl} can be estimated for a concrete, based on its porosity features, then equation no. 15 could be used to predict the time of the initiation period in the model of Tuutti (37).

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6. ALKALI-AGGREGATE REACTIONS

Alkali-aggregate reactions are different from those previously discussed in that the reactive components are usually internally contained in concrete and, therefore, are not dependent on the diffusion of an aggressive solution into the concrete. For appreciable amounts of swelling to occur, however, a source of water is required.

It appears that all aggregates react to some degree with alkalis in cement. In the majority of cases the reactions are beneficial (e.g., increasing the bond between aggregate and hydrated cement paste) or innocuous. In some cases, however, the reactions result in the formation of expansive products which can cause serious cracking of the concrete. The expansion is attributed to the imbibition of water by the reaction products. When cracking occurs its effects can range from being cosmetic (in most cases) to resulting in structural failure (uncommon) of concrete. As discussed in section 3, cracking of concrete even though not causing structural collapse can significantly increase its permeability. Alkali-aggregate reactions may proceed rapidly (several months to a few years) or much slower (e.g., early sign observed only after some 20 to 25 years (54,55,56)). Expansive alkali-aggregate reactions are known to occur with certain siliceous aggregates and certain dolomitic limestone aggregates. Alkali-silica is the most common and well studied reaction and has been found to occur in numerous places in the United States (9) with the greatest abundance of alkali-silica rocks being found in the western states (23). Slow reacting siliceous aggregates have been found in the eastern states. Alkali-carbonate reactions have occurred in some midwestern and eastern states (23).

Cracking of concrete occurs because of the internal development of localized expansive stresses. If the reactive particles are

numerous or of a fine size, more uniformly distributed expansive forces may developed which may result in uniform expansion rather than cracking.

Problems with alkali-aggregate reactions may grow in the future because of large increases in the amount of cement being imported. The alkali contents of the imported cement may not be tightly controlled. Also, in some locations the supply of high quality aggregates has become scarce.

6.1 Alkali-Aggregate Reaction

6.1.1 Mechanism. While the reaction is not thoroughly understood its general mechanistic path appears to be:

(1) Cleavage of silica-oxygen bonds of the silicate network (depolymerization) by hydroxide ions and the dissolution of the depolymerized species. The dissolution of the silica is a function of the pH of the pore solution. A small amount of silica dissolution occurs at the pH (12.5) of a saturated solution of calcium hydroxide but increases by over a thousand-fold at a pH above 13 (13). Sodium and potassium hydroxides are very soluble and the pH of the pore solution of high alkali cements could be as high as 13.6 (57) which would greatly increase the amount of silica dissolved.

(2) Formation of a hydrous alkali silicate gel. This gel is thought by some researchers to act as an semi-permeable membrane (43) which promotes the imbibition of water, leading to its swelling. The swelling further destroys the rigidity of the aggregate and permits the deeper diffusion of hydroxide ions into the aggregate.

(3) As the reaction proceeds, the amount of water imbibed increases as a dilute suspension of colloidal particles is formed which can move from the aggregate into the surrounding matrix. If sufficient amount of expansive products are formed, the resulting internal pressures can cause cracking of the concrete. The extent of the expansion will be limited by the availability of water. However, even in arid regions the internal relative humidity of concrete may be sufficiently high so that reaction products are formed around aggregates (43). If the concrete is sometime in the future exposed to moisture, expansion can occur rapidly.

In addition to the amount of alkalies in concrete and the availability of water, the rate of expansive reaction is also influenced by the properties of the aggregate. Concrete aggregate which are susceptible to expansive alkali reactions are often polycrystallinic and polyminalitic. The reactive mineral may be present in small amounts and its distribution may vary

from aggregate to aggregate. The permeability as well as the size of aggregates can affect the rate of reaction.

6.1.2 Determination of Aggregate Reactivity

Decisions on the potential alkali-silica reactivity of an aggregate are sometimes based on its service records performance. If service records are not available or they indicate that the aggregate may be reactive, laboratory examination and test need to be performed.

The source of aggregates have changed over the years and it is doubtful that sufficient long-term service records exist to form a base for predicting that silica-containing aggregates will be free from expansive reactions for some 500 years.

Laboratory investigation of the potential reactivity of silica-containing aggregates usually consist of petrographic examination, mortar bar test, and chemical test. These methods are briefly analyzed in the following to determine if the individual methods or their combination can be used in predicting the potential expansion of concretes made with silica-containing aggregates. The ACI Guide on Durable Concrete (23) gives a more complete discussion and cites numerous references to detailed investigations.

6.1.2.1 Petrographic Examination. ASTM C 295 (58) provides a standard practice for the petrographic examination of aggregates. It can give information on the potential reactivity of an aggregate based on identification of the minerals present. If present in detectable quantities, presence of the well-known reactive minerals of aggregates may be fairly easily identified by an experienced petrographer. However, some minerals can be present in small quantities which escape detection but which are sufficient to result in concrete cracking.

6.1.2.2 Mortar-bar Test for Potential Reactivity. The ASTM C 227 (59) mortar bar test is the test most generally relied upon to indicate potential alkali reactivity. The test can require up to six months to complete. However, certain metamorphic siliceous rock could require longer test times (possibly up to 3 years) and elevated temperatures to give evidence of expansion (60). If carried out for a sufficient testing period, the test is usually reliable in predicting if an aggregate is potentially reactive. However, studies by Oberholster and Davies (61) suggest that the test does not always give a reliable estimate of the extent of expansive reaction that could occur in field concrete with a potentially reactive aggregate. It is not surprising that the test would not reliably predict field performance because aggregates from even a single source can vary in the type, amount, and distribution of reactive minerals, the degree of crystallinity, size of crystal grains, and the pore

characteristic. Also, the test conditions do not appear to reasonably simulate the range of conditions encountered by field concrete.

6.1.2.3 Chemical Test for Potential Reactivity. This test (ASTM C 289 (62)) is used primarily for a quick evaluation of the potential reactivity of an aggregate. The method measures the amount of silica dissolved in a concentrated sodium hydroxide solution and the reduction in alkalinity. The data is then correlated with aggregate reactivity using standard curves. Results can be obtained in a few days. The results usually correlate with aggregate behavior in the mortar bar expansion test, but it is not suitable for predicting the degree of expansion occurring in concrete (43). The chemical test can be considered to be an aggregate reactivity acceptance test (43).

6.1.2.4 Combination of the Methods. The U.S. Corps of Engineers' Engineering Manual (63) concludes "that none of the available means of evaluation can be relied upon independently, or collectively, to provide an unquestionably positive answer to the problem of potentially harmful reactivity of an aggregate whose constituents include materials capable of reacting with the alkalies in Portland cement." The results of the petrographic examination with corroborating evidence from the mortar-bar test are considered to be the most reliable indicators of potential reactivity. It is further stated that "Spurious results are

possible with the chemical test when certain substances are present in the aggregate being tested." Thus the chemical test should be used in conjunction with the petrographic examination.

Based on the analyses of the predictive capability of the above standard test methods, it appears they do not provide a basis for predicting the long-term expansive characteristics of aggregate containing silica minerals.

6.1.3 Prevention of Alkali-Aggregate Expansive Reactions

Methods for preventing alkali-aggregate expansive reactions are given in detail in the ACI Guide to Durable Concrete (23). They will be briefly discussed herein to indicate the approach for dealing with the problem. Obviously, the best method for preventing the reaction is not to use a reactive aggregate. However, the identification of all reactive aggregates is not, at present, possible. Also, in some cases the only local aggregates which are available are potentially reactive. Another obvious method is to keep concrete dry, which may be virtually impossible to accomplish for 500 years when the concrete is buried in the ground. The use of coatings for concrete to reduce the ingress of moisture is discussed in Appendix A.

Since the alkali-aggregate reaction is sensitive to the pH of the pore solution, designing a low-alkali containing concrete is an effective measure. Often the alkali content is kept low by the

use of "low-alkali" cement (maximum of 0.60% equivalent sodium oxide according to ASTM C 150 (64)). A higher alkali containing cement can be used if the proportions of the concrete constituents are adjusted to give a low alkali content in the concrete. External sources of alkalies must be considered. For example, penetrating groundwater containing large amounts of alkali sulfates could react with calcium hydroxide forming alkali hydroxides. Then, because of the higher solubility of the alkali hydroxides compared to calcium hydroxide, the alkali content of buried concrete will increase. In a few cases (65,66) aggregate has contained appreciable amounts of alkalies and alkali-aggregate reactions occurred even though a low-alkali cement was used.

Many pozzolans have been found effective in reducing expansion due to alkali-aggregate reactions to an acceptable level.

Several mechanisms have been proposed to explain the effects of pozzolans including (43):

- (1) because of their fines, pozzolans react with alkaline hydroxides more rapidly than aggregates and reduce the alkalinity of the pore solution. Also, alkali-pozzolan reactions do not yield deleterious expansive products.
- (2) reduced permeability in the hydrated cement pastes.

(3) partial replacement of a portland cement with a pozzolan containing a smaller proportion of alkalies will result in a reduction of the concrete's alkali content.

Certain fly ashes, silica fumes, and ground blast furnace slags have been found to reduce the expansive reactions. Their effectiveness does depend on their alkali contents. For example, it has been observed that use of a high alkali containing silica fume material increased the mortar-bar expansion compared to the control portland cement (67).

6.2 Alkali-Carbonate Reaction

6.2.1 Mechanism. Although the reaction mechanism is not well understood, it is thought that the reactive carbonate rocks are dolomitic limestone of the general formula, $MgCO_3-CaCO_3$, and contain clay (23). In their reaction with alkali hydroxides, dedolomization occurs (i.e., magnesium carbonate, $MgCO_3$, is liberated) and magnesium hydroxide (called brucite) is formed (ACI 23). The reaction appears to break down the structure of the rock permitting the ingress of water. Then the absorption of water by the clay minerals is thought to take place, which becomes one of the causes of the swelling characteristics of the reaction (68). The affected concrete is most severely cracked in areas where an abundant supply of moisture is available.

6.2.2 Determination of Potential Reactivity of Aggregates

Potentially reactive dolomitic limestones are identified by petrographic examination (ASTM 295 (58)), and the rock cylinder test (ASTM C 586 (69)). In addition, a test method is being developed by ASTM to measure the length change of concrete due to alkali-carbonate rock reaction and a Canadian standard, CSA-A23.2-14A, is available (23).

Definite correlations between laboratory tests and field performance need to be established. Apparently, while the laboratory tests can be useful in identifying potentially reactive aggregates, they do not provide a basis for predicting the rate or extent of expansion in field concrete.

6.2.3 Prevention of Alkali-Carbonate Reaction

ACI Guide to Durable Concrete (23) recommends that the best way to avoid alkali-carbonate reactions is not to use such aggregates. Other ways are to dilute reactive aggregates with nonreactive aggregates (70,71) or to use a cement with equivalent alkali content below 0.40% (23). Unlike with alkali-silica reactions, pozzolans are not effective in mitigating alkali-carbonate reactions except for diluting the alkali content of the concrete.

6.3 Models and Service Life Predictions

Neither a model which mathematically describes the mechanism of alkali-aggregate reactions nor a means for predicting the service life of concrete with potentially reactive aggregates was found in the literature review. Correlations between accelerated laboratory expansion or chemical reactivity tests and field expansions have not been adequately established. Thus there is not a sound basis for predicting the rate or the amount of expansion to be expected using a potentially reactive aggregate in field concrete.

The problem, therefore, cannot be treated as one of kinetics (e.g., reaction rate) but must be treated as a thermodynamic problem. That is, will an aggregate be thermodynamically stable for 500 years in the presence of alkali hydroxides at the concentrations to be expected for concrete buried in the ground? The answer will provide a basis for predicting the service life in the sense that concrete made with a thermodynamically non-reactive aggregate will not experience alkali-aggregate expansive reactions. However, it will not provide a basis for predicting the service life of concrete made with a potentially reactive aggregate.

A test for the reactivity of siliceous aggregates could involve determination of their chemical reactivity with alkali hydroxides. The mechanism of alkali-silica reactions involves

the dissolution of silica and, if a chemical reaction takes place between a siliceous aggregate and alkalies, then, in the absence of calcium ions, the silica concentration of the aqueous solution should increase (57). Determinations of the dissolved silica concentration, therefore, could be used to indicate if the aggregate is thermodynamically stable in the presence of alkalies. The testing procedures would need to be worked out. Also, such questions as what temperature should be used, should the aggregate be reduced to a fine size to expose possible reactive constituents, and what is an appropriate testing time, would need to be answered. Another approach would be to prepare concrete with a higher alkali content than that of the concrete to be used in actual construction, expose it to elevated temperatures and moisture and, after a specified testing time, microscopically examine the aggregates for the development of any reaction products. The presence of reaction products would indicate that the aggregate is reactive. Because almost all aggregates containing siliceous minerals may show some reaction in this test, aggregates of concrete which have been in service for many years without expansion occurring due to alkali-aggregate reactions could be subjected to the test and the extent of reaction determined. This would prove baseline data for evaluating the results of testing potentially reactive aggregates.

7. FREEZING AND THAWING

Freezing and thawing damage (also called frost damage) occurs when a damp concrete is exposed to cycles of freezing and thawing. The concrete does not need to be fully saturated with water for damage to occur as the critical level of saturation is around 85 percent for most concretes (72). Freezing and thawing damage is a serious problem for exposed concrete in the northern states, resulting in its cracking and reduced service life. Horizontal concrete surfaces such as pavements, bridge decks, roofs, sills, and other surfaces where water can remain in contact with the concrete for sometime are especially susceptible to freezing and thawing damage. Several precautions must be taken to avoid freezing and thawing damage, including the incorporation of entrained air in concrete, and proper placement, consolidation, and curing of the concrete.

The concrete structure storing low-level radioactive wastes will be safe from cyclic freezing when they are covered with soil as they will be located below the freeze line. Prior to being covered, however, they could be susceptible to cyclic freezing damage as follows. Immature air-entrained concrete can be damaged if it has not developed adequate strength before being exposed to freezing conditions. Also, if air-entrained concrete is kept in a state of nearly complete saturation so that the entrained air bubbles are extensively filled with water, it may suffer damage from cyclic freezing. This could happen to the

LLW storage structures if water is allowed to pond against them during the construction phase or while they are being loaded with LLW.

Because a potential for freezing and thawing damage does exist for the LLW concrete storage vaults before they are buried, the mechanisms of frost action, factors to be considered in making durable concrete, and applicable models are reviewed.

7.1 Mechanisms

Both the hardened cement paste and the aggregates in concrete can undergo frost damage. The hardened cement paste can be made more resilient to frost damage while little can be done to improve the resistance of an aggregate except to select another aggregate. Therefore, the mechanisms in the hardened cement paste will be discussed in more detail than that for aggregates.

7.1.1 Hardened Cement Paste

Several mechanisms of the freezing process in hardened cement paste have been proposed and the widely accepted mechanisms are discussed herein.

When water freezes in the pore system of hardened cement paste expansive stresses are developed which, if they exceed the tensile strength of the cement, can cause severe cracking. An early explanation developed by Powers (73,74) was that hydraulic

pressures are developed in the pores as water expands in volume by 9% when converted to ice. The resulting expansion causes excess water to move from the site of freezing to adjacent voids. The hydraulic pressures are developed by resistance to the movement of water from the site of freezing. If the voids are not close to the sites of freezing or are not able to accommodate the water, then the hydraulic pressures exceed the tensile strength of the hardened cement paste. This hypothesis indicates that the magnitude of the developed pressure depends on the rate of freezing, extent of saturation and permeability of the paste, and the distance from the freezing site to the nearest air-filled void. Entrained air improves the frost resistance of the paste by decreasing the average distance of the flow-path. The hydraulic pressure mechanism does not account for many of the processes observed when concrete with a predominant amount of small pores freezes. However, it may be active in porous concretes of large interconnected pore systems.

Another explanation developed by Powers (75) and Helmuth (76) is analogous to the mechanism that causes frost heave in soils (see Fragelund for ref.). In this hypothesis, osmotic pressures are developed. Ice crystals formed in the capillary pores are able to attract unfrozen water from gel pores because of differences in free energy between ice and unfrozen water, resulting in the movement of water to the site of freezing. The free energy of the ice (measured by its vapor pressure) is lower than that of

the unfrozen water in the gel pores. The free energy of the ice crystal increases as the free energy of the unfrozen water in the gel pores decreases as the result of the internal desiccation. The ice crystal continues to grow until the free energies are equal. Sufficient osmotic pressures can develop to cause cracking of the hardened cement paste. When the paste contains entrained air bubbles, and the average distance between them is less than a critical size, the unfrozen water preferentially migrates to the air bubbles rather than to the capillaries. By this process the osmotic pressure is reduced to well below the tensile strength of the hardened cement paste.

The relative importance of the two damage mechanisms, development of hydraulic pressure and osmotic pressure, is not unambiguously known. However, it appears that the osmotic pressure mechanism should be most effective in concretes with small pores, such as concretes with low w/c ratios or dense concretes containing pozzolanic admixtures (77). Conversely, the hydraulic pressure mechanisms would probably be active in porous concrete.

A later hypothesis by Litvin (78) suggests that the desorption of water from gel pores is solely responsible for creating hydraulic pressures in the hardened cement pastes and ice formation does not occur in the capillaries.

Regardless of which proposed mechanism is correct, the resistance of hardened cement paste to frost action is known (79) to depend on the spacing of entrained air bubbles, the amount of water in the pores of the paste, the permeability of the paste, the freezing rate, and the strength of the paste.

7.1.2 Freezing in Aggregates. Most rocks have pore sizes much larger than those in cement paste and they expel water during freezing (73). Some aggregates have an appreciable amount of fine pores and if they contain large amounts of absorbed water, severe cracking can occur through ice formation (80). The size of an aggregate can control its resistance to frost damage with frost resistance increasing as its size decreases. A critical size exists below which aggregates can be exposed to freezing temperatures while saturated with water without being damaged (81). A detailed discussion of the effects of aggregates on the frost resistance of concrete is provided by Cordon (79).

7.2 Factors Controlling Resistance to Frost Damage

Factors which should be considered in making concrete resistant to frost damage are briefly discussed herein for concrete structures storing LLW that will be buried underground below the freeze line. The factors covered include exposure conditions, w/c ratio, air entrainment, selection of materials, and curing. A more complete set of recommendations dealing with various types

of concrete structures and exposures are given in the ACI Guide to Durable Concrete (23), and in Durcon (30).

7.2.1 Exposure to Moisture. As previously discussed, if air-entrained concrete is kept in a state of nearly complete saturation so that the entrained air bubbles are extensively filled with water, it may suffer damage from cyclic freezing. The critical saturation level could be exceeded if the concrete is exposed to flowing or ponding water for a lengthy period of time. Thus measures should be implemented during the construction and filling stages to minimize the uptake of water. For example, the geometry of the construction site should promote drainage away from the structure.

7.2.2 Water-Cement Ratio. Frost-resistant normal weight concrete should have a w/c ratio not to exceed the following:

- 1) Thin sections and sections with less than 25 mm of cover over the reinforcement a w/c ratio of 0.40
- 2) All other structures a w/c ratio of 0.45

7.2.3 Entrained Air. The recommendations for air entrainment are for normal strength concretes, with compressive strengths below 55 MPa (8,000 psi). Some problems have occurred with entraining the recommended amount of air and controlling the air

bubble spacing in higher strength concretes, as will be discussed later.

Recommended air contents are given in table 3 for severe and moderate exposures. A severe exposure is defined as a cold climate where the concrete may be in almost continuous contact with moisture prior to freezing, or where deicing salts are used. If the exposure to moisture prior to freezing only occasionally occurs, then the exposure is classified as moderate. The values maybe slightly lowered if the performance of the concrete in a known environment is known. The distance between the air bubbles in the hardened cement paste is very important in obtaining a frost resistant concrete. The air bubbles should have a maximum spacing of 0.4 mm (0.016 in) or a spacing factor of 0.2 mm (0.008 in).

The need for entraining air in high-strength concretes (compressive strengths greater than 55 MPa (8000 psi)) is a controversial issue which is the subject of numerous studies as follows. The resistance to freezing is directly dependent on the capacity of concrete for freezable water and because of the reduced porosity and permeability concretes of low w/c ratios may not have a capacity for freezable water. Therefore, high-strength concretes, should not need entrained air. However, some studies have indicated that non-air entrained high-strength concretes do not perform satisfactorily in laboratory tests (82).

Philleo (16) suggested that low w/c ratio concretes may have no capacity for freezable water if all the available space in the hardened cement paste is filled with hydration products; or the paste becomes so impermeable that saturation by water will not occur. This implies that non-air entrained high-strength concretes could undergo frost damage if they are exposed prematurely to freezing conditions. The review by Philleo (16) is an excellent source of information on the freezing and thawing resistance of high-strength concrete.

7.2.4 Materials and Tests. Whenever a durable concrete is desired, the constituents, (cement, aggregates, and mineral and chemical admixtures) should meet the requirements of the appropriate ASTM specifications. The different types of portland and blended cements, when used in properly proportioned and prepared air-entrained concrete, will provide similar resistance to frost damage.

Most fly ashes and natural pozzolans when used as admixtures produce durable concrete provided that the recommended air content and strength are attained.

The performance of an aggregate should be determined by tests of concrete containing the aggregate. The most widely used laboratory test on the freeze-thaw resistance of concrete is

Table 3. Recommended Air Contents for Frost-Resistant Concrete (23)

Nominal Maximum aggregate mm (size. in.)	Average air content percent ^a	
	Severe Exposure ^b	Moderate Exposure ^c
9.5 (3/8)	7.5	6
12.5 (1/2)	7	5.5
19 (3/4)	6	5
38 (1.5)	5.5	4.5
75 (3)	4.5	3.5
150 (6)	4	3

^a A reasonable tolerance for air content in a field construction is = 1-1/2 percent.

^b Outdoor exposure in a cold climate where the concrete may be in almost continuous contact with moisture prior to freezing, or where deicing salts are used.

^c Outdoor exposure in a cold climate where the concrete will be only occasionally exposed to moisture prior to freezing, and where no deicing salts will be used.

ASTM C 666 (83). It involves subjecting concrete, which is initially saturated with water, to rapid cycles of freezing and thawing. The durability of the concrete is determined by measuring the reduction in its dynamic modulus. The test does not realistically simulate in service conditions. However, the relative performance of aggregates in the test will be predictive of their relative performance in the field, which is of great assistance in selecting aggregates for durable concrete. Some aggregates have been found to only have fair performance in the test but still the concretes made with them have adequate frost durability. If a concrete has a high durability factor after 300 cycles it should be able to withstand a severe freezing and thawing environment. At present C 666 is regarded as the standard test and is most widely used.

Another test, ASTM C 671 (84), has been developed to more closely simulate the moisture and freezing rates encountered in field exposures and is less severe than ASTM C 666. It requires more expensive equipment, which is not commercially available, and may require more time to perform than C 666. The results obtained with C 671 are sensitive to the moisture content of the concrete prior to testing. However, it has been suggested that C 671 is a more realistic test for high strength concrete than C 666 (16).

7.2.5 Curing. Proper curing can be very important because immature air-entrained concrete can be damaged if it has not developed adequate strength before being exposed to freezing conditions. Normal strength air-entrained concrete should be able to resist a few cycles of freezing and thawing when it attains a compressive strength of about 3.45 MPa (500 psi), provided it is not exposed to an external source of moisture. Concrete should attain a compressive strength of 28 MPa (4000 psi) before being subjected to severe freezing and thawing exposure. If the exposure is moderate, then a compressive strength of 21 MPa (3000 psi) should be adequate.

7.3 Models and Service Life Predictions

Three models mathematically describing the mechanisms of frost damage were found in the literature search and are discussed herein. Only one of the models provides a basis for making service life predictions and it is presented first.

7.3.1 Service Life Prediction Model. A model for predicting the service life of concrete exposed to freezing and thawing cycles has been developed by Fagerlund (85). The main aspects of it are outlined in the following. In the model air bubbles are termed "air voids." The spacing of unfilled air voids is treated as a variable because it changes when water is filling the air void system (air void absorption). Frost damage will not occur until the air void absorption reaches a critical value (i.e., the

critical air void absorption) and freezing temperatures are encountered. Methods for obtaining the critical air absorption have been described by Fagerlund based on the air void volume and distribution, and the spacing of unfilled air voids.

The model considers that the complete volume of concrete of a structure rarely fails during one freezing and thawing cycle but occurs progressively, i.e., starting from the outer regions of a volume of concrete, damage spreads inward through many freezing and thawing cycles. The period of service of an element of concrete is the period of time during which the amount of air void absorption in the element is always lower than its critical air void absorption, during periods of freezing temperatures. The service life of the structure is the period of time after which the structure can no longer fulfill its purpose because of frost damage. A structure in constant contact with water and exposed to freezing temperatures will have a finite service life because eventually the critical air void absorption will be exceeded. However, a structure that goes through cycled wetting and drying phases could have a finite or infinite life, with regard to frost damage, depending if the critical air absorption is exceeded while the freezing temperature is reached.

The model is intended to give a means for making a reasonable estimate of the service life of concrete. To make a reasonable service life prediction, relationships for the long-term

absorption process in the air void system must be known as a function of the properties of the concrete, such as permeability, air void volume, and air void distribution. Several examples of service life predictions made by using the model are given by Fagerlund for concrete with non-porous aggregate.

7.3.2 Modeling of Frost Penetration. A two dimensional finite element computer model for predicting frost penetration in saturated aggregates and concrete has been developed by Olsen (86). Based on differential equations for predicting temperature and moisture content, and equations relating freezing temperatures and water potential, the model predicts temperature, depth of frost penetration, water and ice content of aggregates or concrete, and the pore water pressure. The model appears to give predicted values which are in reasonable agreement with experimental data.

The model can be used to analyze the influence of its parameters on the freezing process. For example, the effect of selecting aggregates with different desorption properties on frost durability can be evaluated. However, the model cannot be used for making service life predictions.

7.3.3 Modeling of Freezing and Thawing Processes. Bazant, et al., (87) developed a model which involves the formulation of relationships for sorption isotherms for concrete exposed to

freezing temperatures, diffusion of water, temperature distribution, and internal stresses in the concrete resulting from the freezing of water. The model essentially reduces the freezing and thawing durability problem to the calculation of stresses and strains. Solution of the model would require finite-element computer analysis. To apply the model, information would be needed on the effect of mechanical loading on the freezing and thawing process and on the resulting stresses. In its present stage of development the model cannot be used to make service life predictions.

8. DETERIORATION OF CONCRETE BY LEACHING

Buried concrete in contact with water percolating through soils, e.g., from precipitation, or groundwater, can undergo deterioration by the dissolution of the soluble materials in the hardened cement paste. In this report, the effects of damp soils are taken to be the same as those of groundwater as the mechanisms would be the same and over 500 years the effects may be similar. The concrete vaults storing LLW are required to be constructed above the groundwater table. However, the groundwater table may change over 500 years and, therefore, the effects of leaching by groundwater are covered. Considering the common constituents of portland cement paste, alkali salts are the most soluble followed by calcium hydroxide. The solubility of silica oxide is very low so that the decomposition rate, through dissolution, of the calcium silicate hydrate is very

slow. Leaching can reduce the pH of the concrete as well as making it more porous. Recently, the destruction of a concrete conduit by calcium absorptive acidic groundwater was reported (88). Such cases of complete deterioration are rare because usually the water becomes sufficiently concentrated with the dissolved salt so that a dissolution equilibrium is reached, or the concrete is of sufficient high quality that the rate of leaching is very slow and confined to the surface area. It is doubtful that in the sites selected for the LLW storage structures, that the underground water, by leaching alone, will be able to endanger the structural integrity of the concrete. However, if concrete is exposed to intermediately or continuously flowing underground water for 500 years, other deterioration process could be activated. For example, the amount of dissolution of calcium hydroxide may be sufficient to lower the pH at the depth of reinforcing steel and, thereby, promote corrosion and cracking of the concrete. Thus, the leaching of concrete is addressed in this section. In the following, leaching is confined to direct dissolution processes as opposed to reactions between aqueous solutions with cement reaction products to cause volume changes, such as sulfate attack. Also, it is presumed that the aggregates are inert to leaching.

8.1 Mechanisms

Leaching by water involves the penetration of concrete by water or aqueous solutions, the dissolution of soluble constituents of

the hydrated cement paste, and the transportation of the dissolved species to the underground water reservoir or its flow system.

8.2 Factors Influencing Leaching

The depth of penetration of underground water into the concrete is largely controlled by the permeability of the concrete and the hydrostatic pressure of the water. Assuming a constant temperature, the extent of dissolution is dependent on the chemistry of the water and the amount of soluble constituents in the hardened cement paste, and the mobility of the underground water. If the water reservoir is small and stagnant then it is likely that the concentration of dissolved salts will come in equilibrium with the concrete and the dissolution process will be limited. If, however, the underground water is flowing, then dissolution equilibrium may not be attained and leaching can then be a continuing process. Transportation of dissolved species in concrete is dependent on their migration velocity through the pore system and the flow rate of the ground water.

8.2.1 Permeability of Concrete. The permeability of concrete is clearly one of the most important factors controlling the rate and extent of leaching. Means for decreasing the permeability of concrete have been discussed in section 3.

8.2.2 Underground Water Movement. The flow rate of underground water has been reported (89) to be a major factor in the leaching of a concrete repository for radioactive waste disposal and should be considered in selecting a site. A model has been developed by Atkinson (89) by which the effects of the underground water flow rate on leaching can be predicted. This is discussed later.

8.2.3 Chemistry of Underground Water. Acidic waters will attack concrete through the dissolution and neutralization of the alkali and calcium hydroxides. The rate and extent of the acid leaching is dependent on the acidity of the water, i.e., leaching increases as the pH decreases. Calcium-absorptive acidic soils are especially aggressive to concrete (88). The potential leaching capabilities of ground waters can be related to their Langelier Indexes (also called Saturation Index). The Langelier Index is related to the total solids, total alkalinity, pH, and calcium content of the water (90). A positive index indicates that calcium carbonate will be precipitated; a negative index indicates lime-deficient water (soft water) capable of dissolving calcium from hardened cement paste.

Carbonic acid can be found in some underground waters as a result of the absorption of carbon dioxide by rain, which is most likely to occur around industrial areas, or from the decaying of vegetation. While such waters are usually acidic, they may be

neutralized by reacting with calcareous aggregates but still contain significant amounts of the bicarbonate ion (91). The bicarbonate reacts with calcium hydroxide to precipitate calcium carbonate:



The resulting carbonate-free water can then dissolve calcium carbonate to form more bicarbonate:



so that the process is repeated (92). Through this process, the bicarbonate ion can react with the calcium of the calcium silicate hydrate resulting in its decomposition (92). It appears that water containing more than 20 ppm of dissolved carbon dioxide can result in deterioration of hydrated cement paste (23).

Some soils, such as peat, clay and alum shale may contain iron sulfide (pyrites) which, upon oxidation and in the presence of moisture, produces sulfuric acid (23). The oxidation could occur in excavated soil sites which are left exposed to the atmosphere for lengthy periods. Also, underground water may become acidified with sulfuric acid by drainage through mines or mining tailings, or by coming in contact with industrial waste.

A dense concrete with a low w/c ratio should be able to resist most underground waters. If the underground water is acidic but stagnant, the use of limestone aggregate should be considered. In the unlikely case that a site is selected with flowing underground water that is highly acidic or highly calcium-absorptive, a low permeability concrete with limestone aggregate may not be sufficiently durable. In such a case, an appropriate surface coating must be used (Appendix A). The analyses of soils and groundwaters would indicate the need for special precautions.

8.2.4 Chemistry of Hydrated Cement Paste. The constituent of hydrated portland cement paste that causes the most severe problems through leaching is calcium hydroxide. A typical hardened portland cement paste could contain between 20 and 25% calcium hydroxide by volume (93). The leaching of a portion of the calcium hydroxide would result in a porous matrix with an increase in permeability. If a severe leaching condition exists, the amount of calcium hydroxide in the paste could be decreased by the addition of a pozzolan. However, the effect of the reduction in calcium hydroxide on the stability of the calcium silicate hydrate would need to be determined.

8.3 Models and Service Life Predictions

Atkinson (89) developed a model to estimate the pH change occurring in the concrete of nuclear waste repositories by leaching the constituents of the hydrated cement paste by

groundwater. This model deals with the chemical state of the hydrated cement paste and does not consider the structural integrity of the concrete structure. In this model the repository is approximated as a sphere of equal volume to the actual repository. The fractional release rate (dF/dt) of any component of the concrete into the groundwater is related to the flux density of the groundwater (J_o), and the concentration of the component in the pore solution (C_l) and its initial solid concentration in concrete (C_o):

$$dF/dt = 3/4 (J_o C_l / R C_o) \quad (18)$$

where R is the radius of the concrete sphere. At very low flow rates, the loss is controlled by diffusion to the surrounding geology characterized by an intrinsic diffusion coefficient.

The groundwater flux density is determined by the hydraulic gradient (h/L) and the hydraulic conductivity (K) of the geological environment in which the repository is located:

$$J_o = K(h/L). \quad (19)$$

The flux density, J_o , is the volume of water crossing unit area of ground in unit time and has units of $m s^{-1}$. It is often referred to as the groundwater flow rate ($m^3 s^{-1}$ per m^2 section) (89). Ranges of hydraulic conductivity and corresponding

flux for a 1% hydraulic gradient, indicate that an "average" value for groundwater flow rate could be taken to be $10^{-11} \text{ m s}^{-1}$ (89). According to Chapman, et al., (94) groundwater around a "typical repository" could have a flow rate of up to $10^{-10} \text{ m s}^{-1}$, whereas groundwater in a fast aquifer flows at 10^{-6} m s^{-1} . Based on the model, the effects of groundwater flow rates on the fraction of calcium released from concrete is shown in Fig. 10. Considering the flow rate and chemistry of the ground water, and the chemistry and the permeability of the concrete, the model predicts that the groundwater flow rate will have the largest effect on the service life of concrete.

The pH of the concrete is an indicator of its chemical state as it is subjected to leaching by groundwater, as schematically represented in Fig. 11. Initially the pH is above 13 due to the alkali hydroxides in the concrete pore solution. After the alkali hydroxides have been removed by leaching, the pH is controlled at 12.5 by calcium hydroxide. When the calcium hydroxide is depleted, the Ca/Si ratio of the calcium silicate hydrate (CSH) begins to decrease; when the ratio of 0.85 is reached, the pH is 10.5. During the final dissolution stage, the low Ca/Si calcium silicate hydrate dissolves congruently at a pH of 10.5 until it is consumed. When the calcium silicate hydrate is completely dissolved the pH will be either that of the groundwater or of any residual salts in the original concrete (89, 91).

The reduction of pH of a structure, with a radius of 20 m, and a reference concrete with a portland cement content of 185 kg m⁻³, caused by a groundwater flux density of 10⁻¹⁰ m s⁻¹, as a function of time is shown in Fig 11. According to the model predictions, the pH will be above 10.5 for about 4x10⁶ years in the mass of concrete. In this calculation, the permeability of the concrete was taken to be the same as the ground. Also, the model predicts that a pH front of 10.5 will move towards the center of the concrete at a rate of 1 m for every 1.5x10⁵ years.

The effects of groundwater containing 10⁻² molar of "reactive species" was estimated by the model to decrease the time for the pH of the concrete to be reduced to 10.5, by a factor of four compared to "nonreactive" groundwater. The major contributor to the concentration of the reactive species was the bicarbonate ion (95). Therefore, the model predicts a pH of 10.5 could be experienced by concrete lying at a depth of 1 m from the surface in about 3.5 x 10⁴ years, when exposed to the above conditions of groundwater flow and salt concentration. Although these estimates are rough they do suggest that good quality concrete should not be directly degraded by groundwater in less than 500 years if the groundwater is flowing at a rate not exceeding 10⁻¹⁰ m s⁻¹.

An analysis of relationships between groundwater flow and pH of concrete indicates that under certain conditions the passivation

film on reinforcing steel can be destroyed. According to Fig. 11, the calcium hydroxide of the mass concrete (20 m sphere) can be completely depleted in about 10^5 years, which translates into a reduction of the pH to below 12.5 at the depth of 100 mm in around 500 years. If the groundwater contains 10^{-2} M of reactive species, then the estimated time is only 125 years. Therefore, under the above conditions, reinforcing steel placed at 100 mm below the surface of concrete may be exposed to a pH of less than 12.5 within 500 years of construction.

9. OTHER DETERIORATION PROCESSES

Deterioration processes which usually are not a problem during the normal 50 to 100-year service life of concrete structures may become more serious as concrete exceeds this life span. Two examples of such possible processes are presented in this section. In addition, deleterious substances may be present in the LLW which can attack concrete and such materials are briefly discussed.

9.1 Microbiological Attack

Sulfate producing bacteria, such as *Thiobacillus thiooxidans*, are capable of oxidizing elemental sulfur and sulfides (e.g., iron sulfate, pyrite) to sulfuric acid in a relatively short

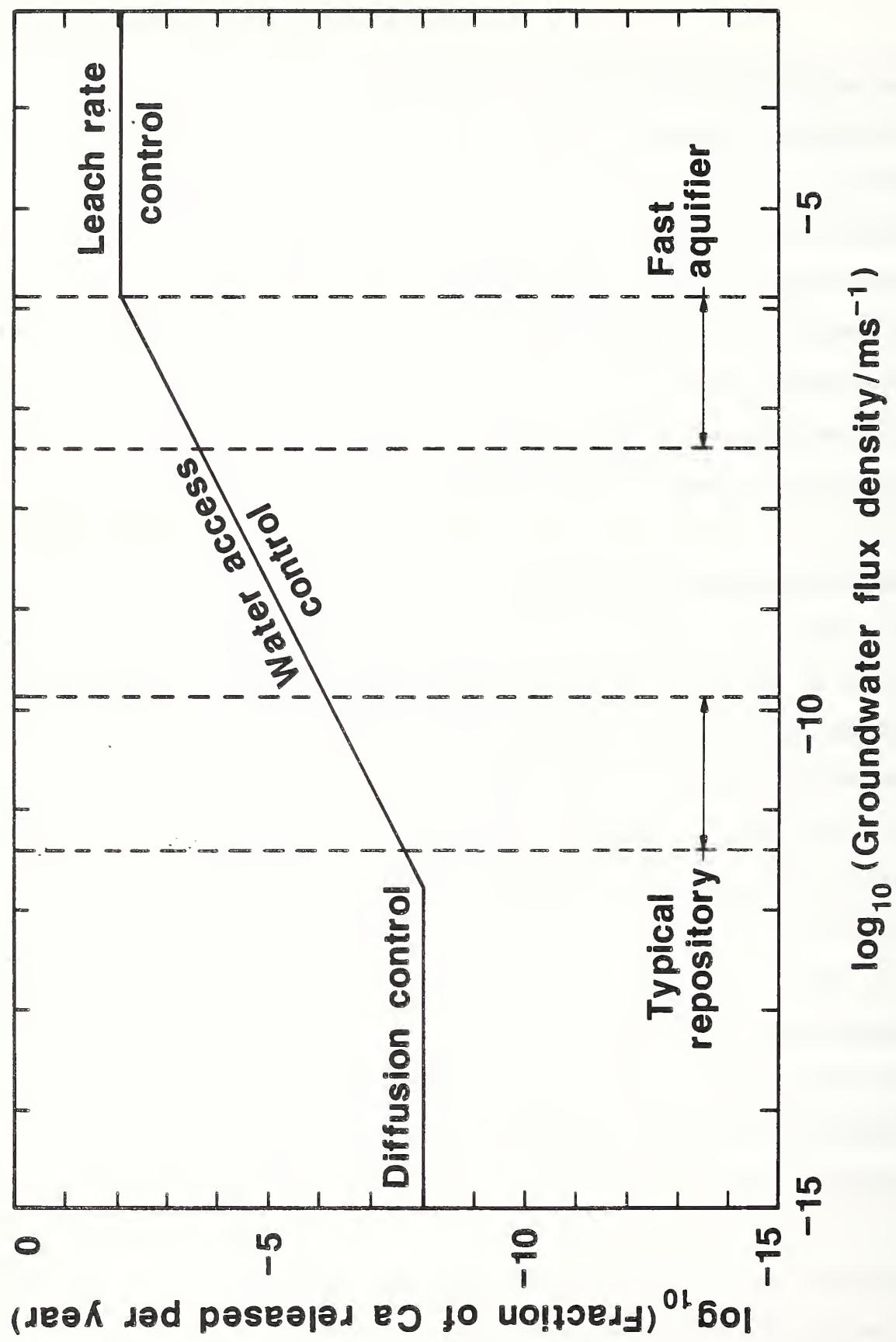


Figure 10. Estimated fraction of calcium released per year from concrete by groundwater (89).

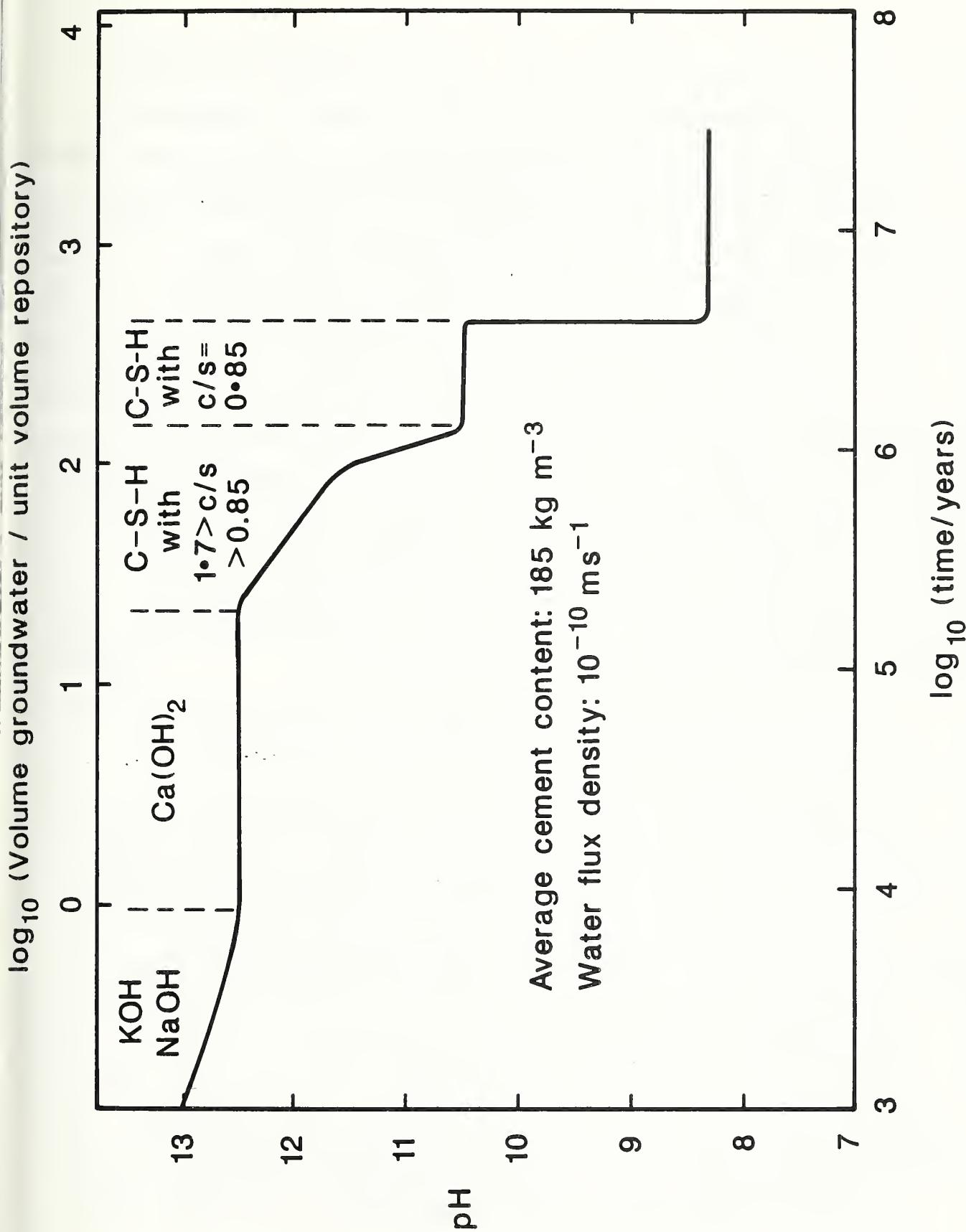


Figure 11. Estimated time dependence of pH with concrete exposed to groundwater (89).

period under aerobic conditions (92). Aerobic conditions could exist during the period when the LLW storage site is excavated. This process can acidify the groundwater which can deteriorate concrete by an acid reaction as well as by sulfate attack. Some bacteria can attack concrete by transforming ammonia into nitrites and nitrates or by producing lactic acid and butyric acid. In the normal design life span of concrete, bacterial action does not appear to be a major cause of concrete deterioration by itself, but can tend to make groundwater more deleterious to concrete (92). It is difficult to predict whether bacterial activity over 500 years will have much effect on buried LLW concrete vaults. If necessary, the examination of buried concrete vaults possibly could give useful information on the long-term potential effects of bacteria activity.

9.2 Salt Crystallization

Dissolved soluble salts can be precipitated in the pores of porous materials as a result of water evaporation. If the pores are filled with salt crystals, further crystal growth can result in the development of internal stresses. If these stresses exceed the tensile strength of the material, cracking can occur. Salt crystallization damage is usually a slow process occurring near surfaces where evaporation takes place. It is a major cause of stone deterioration (96). Recently, Sayward (97) suggested that salt crystallization can make a significant contribution to the deterioration of concrete. Salt damage would most likely be

Table 4. Composition of Some Natural Groundwaters (95)

	Granite	Sandstone	Shale	Limestone	Dolomite
pH	7.0	8.0	7.3	7.0	7.9
pNa	3.4	3.3	2.6	3.0	3.5
pK	4.0	4.0	4.2	3.7	--
pCa	3.5	3.0	2.5	2.7	2.8
pMg	3.8	3.5	2.5	3.4	2.8
pH ₄ SiO ₄	3.2	3.9	3.5	3.7	3.4
pHCO ₃	2.9	2.6	2.1	2.3	2.2
pCl	4.0	3.7	4.0	3.2	3.3
pSO ₄	4.2	3.2	2.2	3.4	4.7
-log (ionic strength)	2.8	2.4	1.7	2.2	2.2

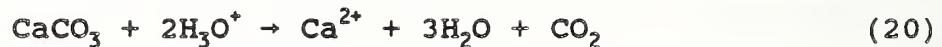
pX denotes minus logarithm (to base 10) of the concentration of X in mole litre⁻¹.

found on the inner walls of buried concrete structures, where evaporation of a salt solution would be expected to take place. Significant salt damage could be anticipated if permeable concrete is exposed to rapidly flowing groundwater which is laden with salts.

9.3 Attack by LLW

The most likely constituents of LLW to attack concrete are those which are acids or which can form acids upon hydrolysis or

oxidation. Both inorganic and organic acids will react with the calcium hydroxide of hydrated cement pastes and thus reduce the pH of the pore solution and, if present in sufficient amounts, destroy concrete. Organic substances such as alcohols, aldehydes, and phenols can produce acidic solutions which can attack concrete. The stronger acids will attack concrete the most rapidly. However, over a long period of time the extent of attack will be primarily dependent on the amount of acid present. If acid attack is anticipated, the use of a calcarious aggregate should be considered because, in principle, calcium carbonate will neutralize an equivalent amount of acid:



Lists of a variety of inorganic and organic substances which are known to attack concrete are given in Appendix B.

10. EMPIRICAL KINETIC MODELS

During the 1986 CEB/RILEM Workshop on Durability of Concrete, kinetic models for many of the common deterioration processes of concrete were proposed (98). These models are essentially empirical models which need confirmation. Sub-models need to be developed to solve these models similar to the sub-models developed by Tuutti (37) for solving his corrosion model. Nevertheless, they demonstrate what is generally known about the

differences in the reaction patterns of the deterioration processes.

Mathematical models for carbonation, chloride penetration, corrosion, frost attack, sulfate attack, and alkali-aggregate reactions are given in table 5. The progress of deterioration (in arbitrary units) are represented in Fig. 12. This figure is intended to show only the general shape of the plots of deterioration versus time and do not indicate relative deterioration rates.

The curves for sulfate attack, alkali-silica reaction, corrosion of reinforcing steel, and frost attack all exhibit an induction period which is controlled by the rate of penetration or diffusion of water or aqueous solutions in concrete. This observation is consistent with the mechanisms described in the sections dealing with a more detailed discussion of the respective deterioration processes. Information on the relative time of the induction period compared to the time for failure after the initiation (t_0 in Fig. 12) is very desirable. It is possible that if the induction period controls the deterioration rate that data on penetration or diffusion rates could provide a sufficient basis for estimating service lives.

11. RECOMMENDED RESEARCH PROGRAM

The recommended research program is based on the analysis of the deterioration processes that are considered to be serious problems for concrete buried in soils. Of the major processes covered in the review part of this report, only freezing and thawing does not appear to need further exploration in the LLW underground storage program. Freezing and thawing is not likely to be a problem if the concrete structures is covered with soil and is below the freeze line. If the recommendations given in Section 6 are followed, then the likelihood of freezing and thawing damage occurring is minimal. At the present level of the knowledge of alkali-aggregate reactions, it does not appear likely that the service life of concrete containing potentially reactive aggregates can be predicted with any confidence. It is recommended that a test be developed, as outlined in Section 5.3, to determine the potential alkali reactivity of an aggregate.

None of the presently available test methods nor the present level of knowledge of alkali-aggregate reactions are adequate to provide a basis for giving a reasonable level of assurance that a potentially reactive aggregate will not undergo a severely deleterious reaction within 500 years after construction.

Candidate concretes for evaluation are discussed first, followed by a recommended approach for predicting the service life of concrete buried underground. All foreseeable deterioration

Table 5. Durability of Models (98)

Form of Attack	Model	
Carbonation	$x = kt$ where $k = (c D) / b$	[1]
Chloride penetration	$x = kt$ where $k = (c D) / b$	[2]
Corrosion	$x = t_0 + kt_1^a$ where $t_0 = kt$ in Eq. [1] or [2] $a = 0.5$ for diffusion control $a = 1.0$ for reaction control	[3]
Frost attack factors	$N = t_0 + K_e R$ where N is the number of cycles, and K_e and R define environmental and resistance respectively	[4]
Sulfate attack	$x = t_0 + kt_1^a \quad a > 1$	[5]
Alkali-silica reaction	$x = t_0 + kt_1^a \quad a > 1$	[6]

a The undefined parameters are:

K is the rate constant,
t is time,
R is a constant
b is the reserve porosity,
D is the diffusion constant, and
 t_0 is the initiation time

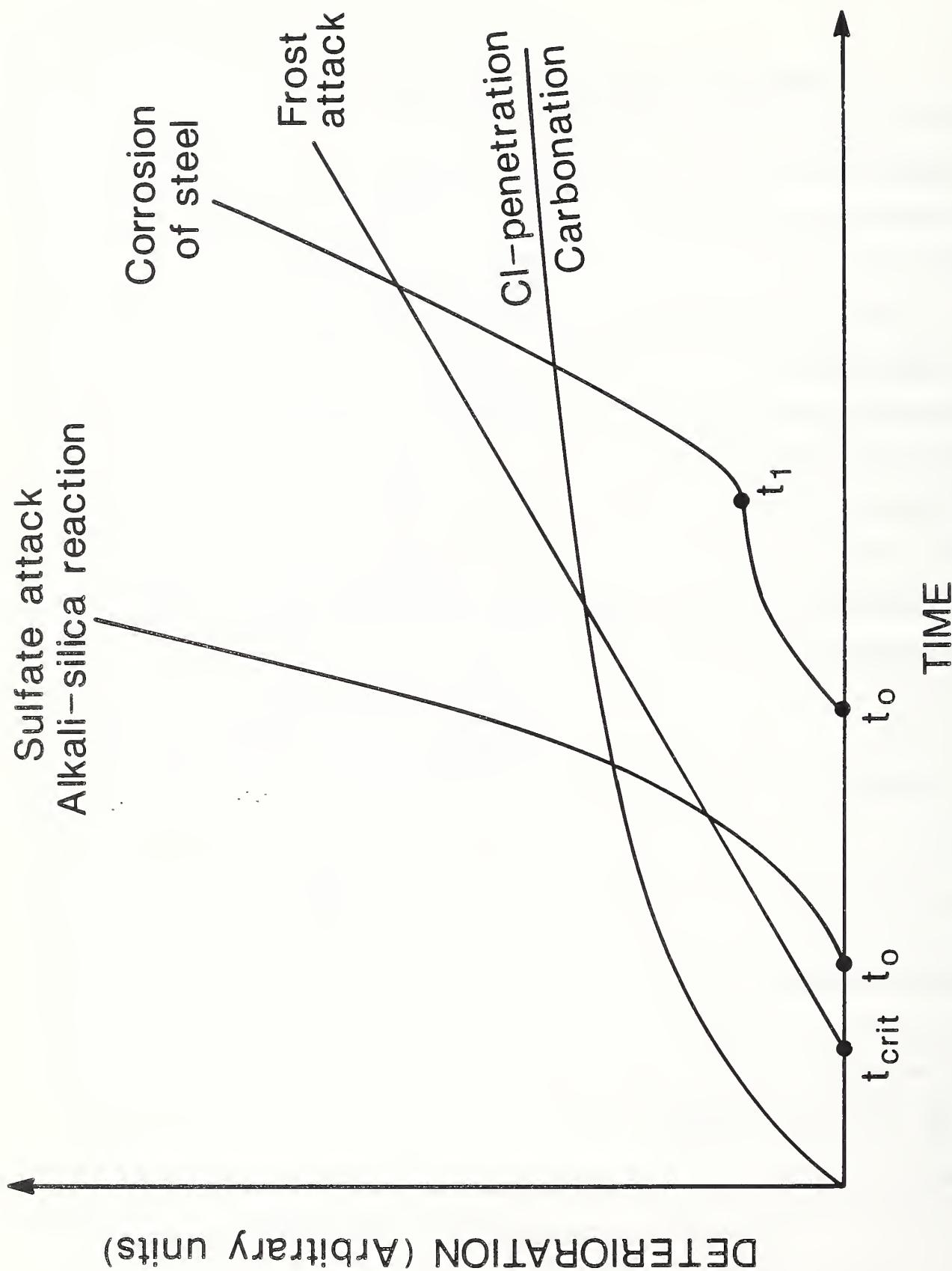


Figure 1.2. Typical rates of deterioration. Meanings of t 's are given in table 5.

processes are addressed, including sulfate attack, corrosion of reinforcing steel, leaching by groundwaters with various mineral contents, and the synergistic effects of combinations of chloride, sulfate, carbonate salts, and acids.

11.1 Candidate Concretes

Two different approaches (they can be combined) can be followed in the design of concrete for constructing underground vaults for storing LLW: 1) select cements and aggregates which have mineralogical compositions that minimize aggressive chemical attack; and 2) design dense concretes with low porosities and permeabilities. Often the first approach, combined with some reduction in permeability, is followed in designing durable concrete with normal lifetimes (less than 100 years). This approach is often satisfactory if high quality concrete is produced and if the service conditions are the same as those considered in designing the concrete.

The second approach is made more feasible by recent developments in concrete technology. As discussed in Section 3, very low porosity concretes can be produced by combinations of high-range water reducers (superplasticizers), suitable pozzolans, silica fume, and dense impermeable aggregates. A standard test does not exist for measuring permeabilities of concrete and their compressive strengths are often used as a measure of relative permeabilities: both the permeability and compressive strength of

concrete are improved by reduction in porosity, thus high-strength concretes tend to have lower permeabilities than normal-strength concretes. It is recommended that although concretes are classified in the following on the basis of strength, research on relationships between moisture movement in concrete and service life should be performed, which would involve developing an acceptable method for measuring factors controlling moisture movement in concrete, e.g., permeability. Based on the differences in materials and technologies for preparing high-strength concretes, three permeability levels, based on compressive strength classifications, are proposed for study: 1) Class I, compressive strength below 70 MPa (10,000 psi); Class II, compressive strength roughly between 70 MPa (10,000 psi) and 103 MPa (15,000 psi); and Class III, with compressive strengths above Class II. Class I includes conventional concrete and would be tested to provide a basis for determining the improvements obtained with the more impervious concretes. Also, this would facilitate comparisons of the large amount of data for conventional concretes in the literature with the performances of Classes II and III concretes.

Class II concretes can be readily prepared by ready-mixed concrete companies. Class III concretes are becoming commercially available. For example, a structure is being constructed in Seattle, Washington (99) using ready-mixed

concrete with a compressive strength of approximately 138 MPa (20,000 psi).

11.2 Recommended Approach for Predicting Service Lives

The principle methods for predicting the service life of concrete that were disclosed in the review and presented in this report are based on experience, accelerated testing, mathematical modeling based on understanding the chemistry and physics of deterioration processes, and empirically-derived correlations. It is recommended that a combination of accelerated testing and modeling be used to predict the service life of concrete selected for underground storage of LLW.

A recommended practice for the development of accelerated short-term tests which can be used for the prediction of service life is given in ASTM E632 (5). The following discussion of the application of the practice is based on reference no. 6. The practice consists of four main parts (Fig 13): 1) Problem Definition; 2) Pre-Testing; 3) Testing; and 4) Interpretation and Reporting of Data.

In Part 1, referring to the numbered boxes in the chart, the first step (Step 1) is to define the performance requirements for the material or component in service and to set performance criteria which must be met. These criteria provide an objective basis for selecting materials. In Step 2, the material should

be characterized in terms of its constituents and interfaces between the constituents. Concrete should be characterized in terms of its composition and mixture proportions, mechanical properties, permeability, the chemistry and microstructure of the hardened cement paste, and the mineralogy of the aggregates. Critical performance characteristics are specified in Step 3; these characteristics will be used in delineating the limiting condition below which the material or component is deemed unserviceable. For example, failure criteria for the concrete of LLW storage vaults may be 1) the corrosion of reinforcing steel, 2) the deterioration of 50% of the concrete, or 3) the movement of sufficient groundwater through the concrete to attack the LLW containers. In Step 4, the expected ranges of degradation factors to which the material or component is likely to be exposed in service are identified. For example, to develop an accelerated test for sulfate attack for underground buried concrete, the range of the concentrations of sulfates in the groundwater, at the different sites, needs to be known. Possible synergistic effects between degradation factors must be identified. An example of a synergistic effect is the combined influence of groundwater flow and groundwater chemistry on the service life of concrete (discussed in Section 8). The identification of the possible deterioration processes, Step 5, is needed to develop simulative accelerated tests. With the knowledge obtained in Steps 1 to 5, it may be postulated how the degradation process can be accelerated. If degradation can be

PART 1 - PROBLEM DEFINITION

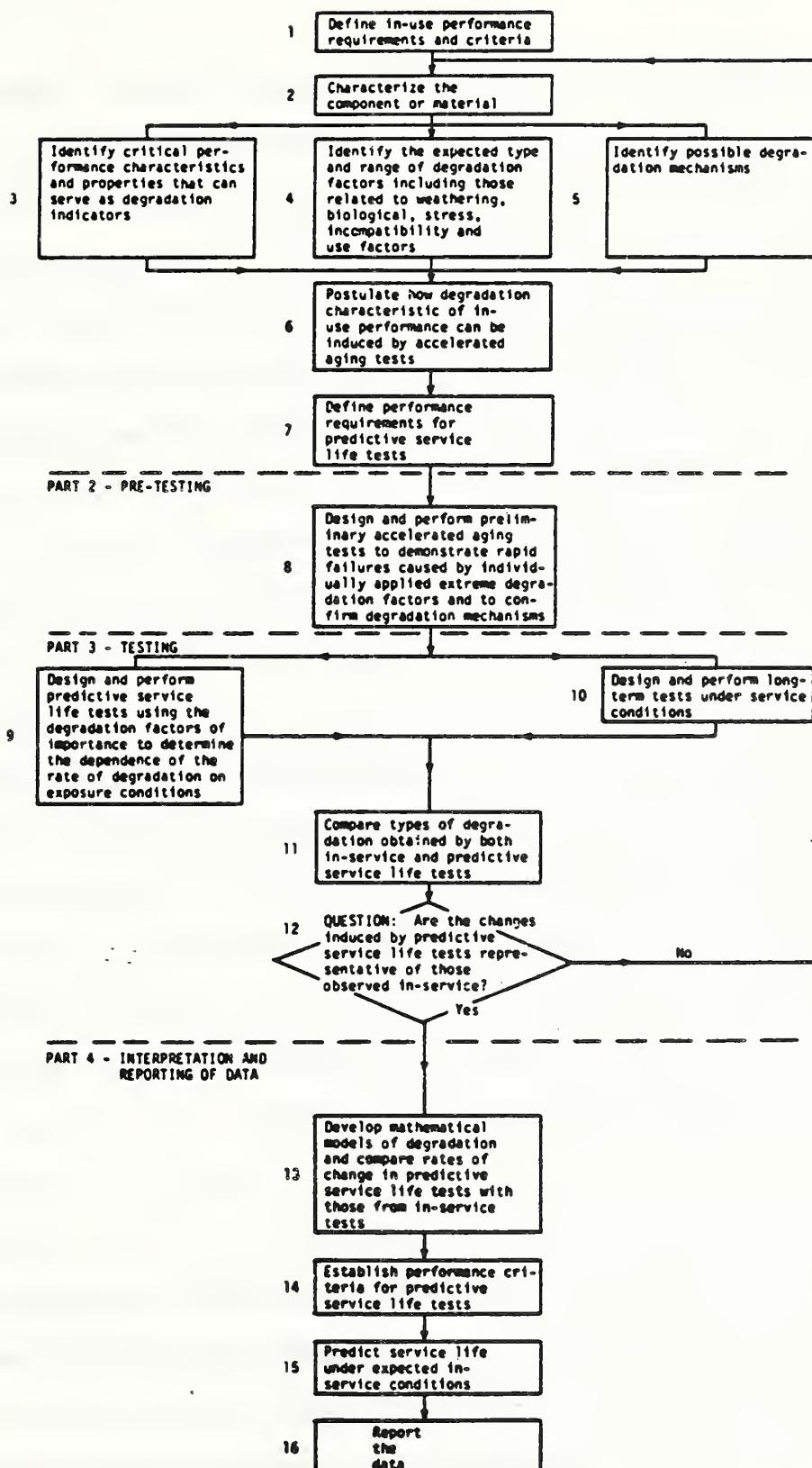


Figure 13. Methodology for developing and using accelerated tests in predicting service lives (5).

accelerated without changing the mechanism of failure, then laboratory test time can be reduced. Once the experimental procedure has been determined, the performance requirements for the test specimens can be stated (Step 7). It must be recognized that much of the knowledge may not always be available. In such cases, assumptions based on the best available opinions and experience should be made. Part 1 is largely completed for concrete storing LLW underground by the information contained in the present report. However, further improvements in the understanding of relevant deterioration processes is urgently needed.

When Part 1 is completed, Part 2, Pre-testing, can be started (Step 8). Its purpose is to demonstrate that rapid failure can be caused by intensifying the factors specified in Part 1. If it is previously known that rapid failure can be induced, then this step can be deleted. Increases in the concentration of sulfates in groundwater is known to increase the rate of sulfate attack on concrete and thus does not need to be explored.

Accelerated durability testing is carried out in Part 3 (Step 9). At the same time (Step 10), long-term tests under in-service conditions should be initiated. The results of long-term tests provide the most convincing evidence that the results of accelerated tests can be extrapolated to in-service conditions. In the case of developing methods for predicting the service life

of concrete for LLW underground vaults, the performance of in-service concrete structures exposed to groundwater or to flowing surface waters could be investigated and the results compared with the results of the accelerated tests. If the data from in-service concrete is consistent with the predictions from accelerated tests then confidence in the extrapolations is significantly increased.

If the results of the accelerated tests and long-term tests are consistent with each other, Part 4, Interpretation and Reporting of Data, should be undertaken. This includes use of experimental data to predict the course of deterioration under expected in-service conditions (Step 13) and to predict the time at which failure, as defined by the performance criteria, will occur (Steps 14 and 15). Mechanistic mathematical models are developed in this Part to describe deterioration processes and to relate the rates in accelerated tests with those of long-term in-service tests. The final step (Step 16) involves reporting the data with clear and explicit statements of the assumptions used in developing the models.

It is recommended that the methodology given in ASTM E 632 be followed in developing accelerated tests and procedures for predicting the service life of concrete.

11.2.1 Accelerated Testing

Concrete deterioration processes which are likely to be important in LLW storage are largely controlled by the ingress of aggressive solutions into the concrete. For this reason, laboratory experiments should be aimed at developing data on penetration rates which are needed for estimating the concentrations of aggressive species accumulating with time in any volume element of the concrete. Diffusion and permeability data will be needed for predicting the service lives of concrete exposed to sulfates, chlorides, and carbonates, and to ground waters with a negative Langelier Index and/or with an acidic pH. Because the permeability coefficients in good quality concrete are low ($<10^{-10} \text{ m s}^{-1}$), acceleration will be required to obtain penetration rates which can be used in the present study.

Possible methods for accelerating the penetration of aqueous solutions into concrete include increasing the temperature, using a series of concentrations of attacking species which range from expected in-service concentrations to concentrations substantially above the "worst case", forcing solutions into concrete by application of hydrostatic pressure, and cycles of wetting and drying.

Relationships between the depth of penetration at in-service conditions and penetration results from accelerated testing can be evaluated by application of a modified form of the time

transformation function, $p_i(t)$, which is normally expressed in the equation (100):

$$F_i(t) = F_o(p_i(t)) \quad (21)$$

where t is time, $F_i(t)$ is the life distribution at the i 'th accelerated stress level, and $F_o(t)$ is the life distribution at the in-service stress level. In the modified form, $P_i(t)$ is the distribution of the depths of penetration with accelerated stress i , and $P_o(t)$ is the distribution of depths of penetration under in service conditions:

$$P_i(t) = P_o(p_i(t)). \quad (22)$$

The penetration-time transformation function can be obtained by using a range of elevated stresses, where dissolved salts in groundwater, temperature, hydrostatic pressure, and wetting and drying cycles are examples of environmental stresses. An example of the use of the penetration-time transformation function to predict the depth of penetration at service stress S_0 is shown in Fig. 14. In the figure, the depth of penetration for a threshold concentration is plotted versus time for stresses above the service stress. When the threshold concentration has penetrated to a critical depth, either failure has occurred or the failure process has been initiated.

The time transformation function approach is applicable if the deterioration mechanism under all tested stress levels is the same as that taking place at in-service conditions (100). Also, it is assumed that deterioration begins at the instant of stress application and that deterioration is an irreversible cumulative process. Once a well-behaved penetration-time transformation function is obtained, it can be used to predict the depth of penetration into concrete as a function of time at LLW storage sites. To be of general use, transformation functions will need to be obtained for the range of concretes used in construction of the storage structures. If a relationship can be derived between the function and some concrete parameter or property (e.g., w/c ratio, compressive strength, porosity, or permeability) then values for the time transformation function can be extrapolated from a few concretes to a wider range of concretes.

Synergistic effects may develop between deterioration processes, e.g., sulfate attack and corrosion (101). It is recommended that the importance of synergistic effects be assessed by the combination of time transformation functions for different processes with a time synergistic function, and using a multivariable analysis (100).

11.2.2 In-Service Concrete Studies

Adequate long-term testing can require many years of exposure, especially when attempting to predict the service life of

concrete which is intended to remain in service for 500 years. Investigation of the performance of in-service concrete can supplement or possibly provide an alternative to long-term testing that is based on companion specimens to those of the accelerated testing program. It is recommended that specimens be taken from in-service concrete structures exposed to groundwater or to flowing surface water. Depth of deterioration and the depth of alteration in the microstructure and chemistry of specimens can be determined by light and scanning electron microscopy.

Even though the concretes from the in-service structures may differ from those in the accelerated testing program, they could provide valuable information on the type and extent of concrete deterioration which can be anticipated. If the concrete and service environment are adequately characterized, the data on depth of penetration and extent of deterioration could be used to test if the models give at least qualitatively reasonable predictions.

11.2.3 Models for Service Life Prediction

Once the values for the inputs are known, models can be used to predict the service life of concrete. The type of model developed by Tuutti (37) for corrosion predictions is well-suited for the present study. By coupling it with penetration data obtained from accelerated testing, estimates of the service life of reinforced concrete could be obtained. It is recommended that

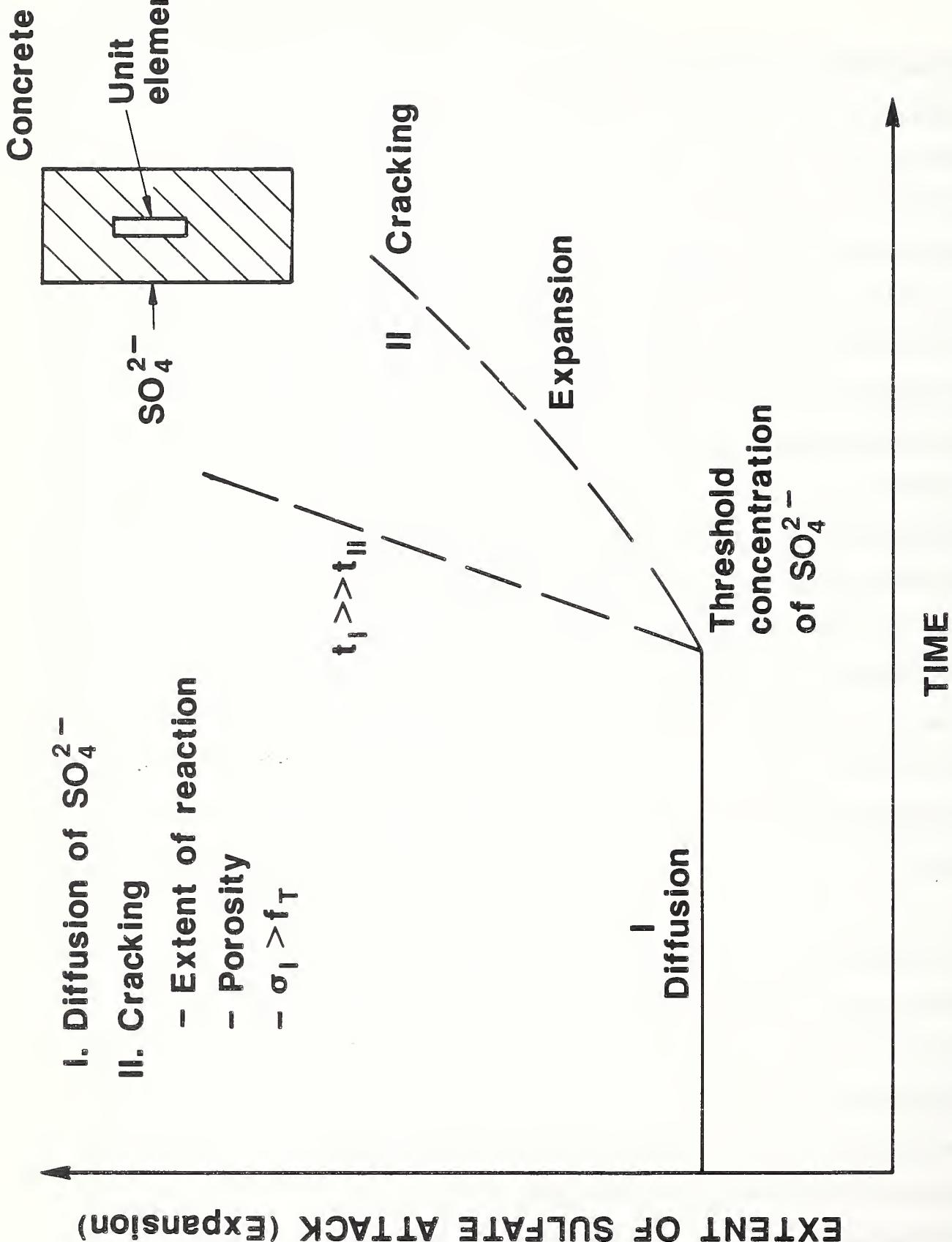


Figure 14. Schematic of proposed conceptual model of sulfate attack, by ettringite formation, of concrete.

the development of a similar type of model be undertaken for sulfate attack, which could be coupled to penetration data obtained from accelerated testing.

A proposed model for predicting the service life of concrete subjected to sulfate attack is presented in Fig. 14. It consists of two major mechanistic steps: Step I, diffusion of sulfate ions to an unit element in a concrete component; and Step II, the expansion and cracking of the unit element of concrete due to the formation of ettringite. Step I is completed when the threshold concentration (concentration of sulfate ions required to cause concrete expansion through ettringite formation) is reached at the unit element of concrete. Thus in Step I, ettringite formation is initiated. When no further ettringite crystals can be accommodated in the pore volume, expansion will start (beginning of Step II). Cracking will occur when the internal stresses (σ_1) exerted by ettringite formation exceed the tensile strength (f_T) of the concrete. Failure is considered to occur when the unit element cracks. If the time for the completion of Step I is much greater than that for Step II, then the prediction of service life is reduced to only considering Step I. Even if only Step I needs to be modeled, determination or estimation of penetration rates is not sufficient, by itself, to predict the service life. The model must also be capable of predicting if a sufficient amount of

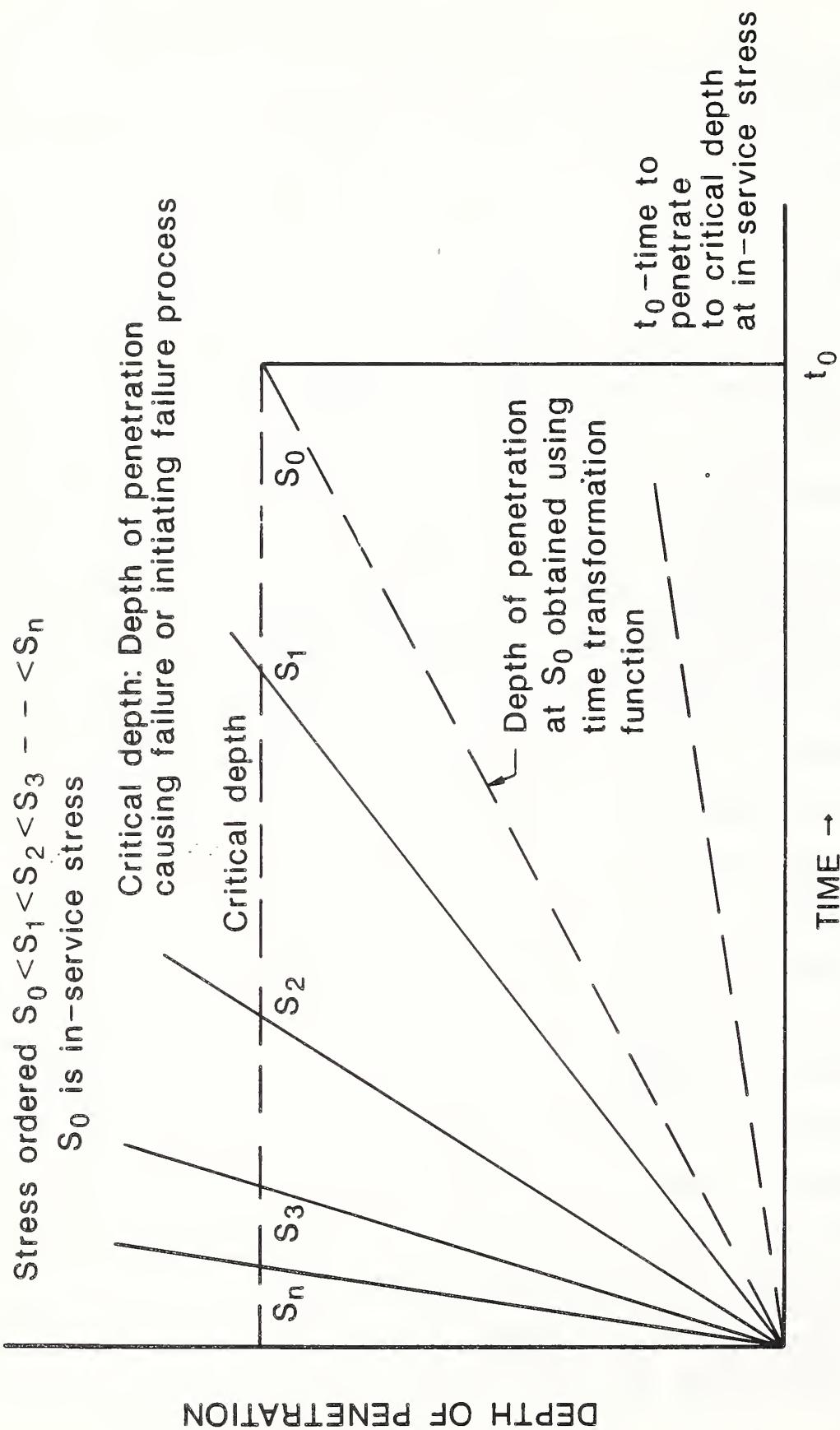


Figure 15. Method for predicting the advance of threshold concentration of aggressive solution concrete at in-service stresses, S_0 , based on elevated stresses, S_m .

ettringite will be formed by the sulfate - tricalcium aluminate reaction to cause cracking. Otherwise the model may falsely predict failure when the tricalcium aluminate content of the cement is too low to induce cracking.

The model developed by Atkinson (89) for leaching by groundwater should be further evaluated to determine if it gives, at least, reasonable service life predictions. Also, recommendations should be developed on the acceptability of sites based on their groundwater flow and chemistry, including their Langelier Index.

11.3 Research Priorities

Based on analyses of the likely deterioration processes of concrete buried underground and the factors controlling their rate, the following research priorities, in order of decreasing importance are recommended:

- 1) Determination of penetration rates of sulfate, chloride, and carbonate ions and acids in candidate concretes. By using a modified time transformation function estimate the penetration rate at in-service stresses from penetration data obtained at elevated stresses. Predict service lives based on time required for specific concentrations to reach critical (failure) depth.
- 2) Develop mathematical model to predict service life of concrete exposed to sulfate ions, based on conceptual model schematically presented in Fig. 14. Model considers both rate of sulfate penetration and the rate of expansive reactions. Use the

penetration data obtained in Item 1) to solve the sulfate model. Validate model by predicting depth of sulfate attack of in-service concrete.

3) Develop method for determining potential alkali reactivity of aggregates. Validate method by testing aggregates of in-service concrete showing reactive and apparent unreactive aggregates.

4) Determine reliability of mathematical models for predicting service lives of concrete subjected to corrosive environments and concrete exposed to leaching conditions. If necessary, modify existing models or undertake development of new models.

5) Carry out service life evaluation of barrier coating systems for concrete using accelerated testing methodologies.

6) Investigate joint systems. The possibility of either avoiding or reducing the amount of joints should be evaluated by a stress analysis. Also, the use of prestressing tendons should be considered in the analysis. Carry out service life evaluation of the selected joint system or its alternative.

The first four research priorities are aimed at identifying concretes which will have reasonable probabilities of having service lives of at least 500 years. The fifth research priority reflects the reality that even good quality concrete can crack. However, the use of protective coatings does not convert a poor quality concrete into a high-performance concrete. Joints may be a weak link in a structure once high quality concrete is

obtained. It appears that joint materials have short service lives.

12. SUMMARY AND CONCLUSIONS

In this report, the major deterioration processes that concrete of underground LLW storage vaults will need to resist are identified and analyzed. These processes are sulfate attack, corrosion of reinforcing steel, alkali-aggregate reactions, and leaching by underground water. Freezing and thawing damage could occur before the vaults are covered with soil. Other deterioration processes which could occur are microbiological attack, salt crystallization, and attack by LLW forms, especially acids.

All of these processes involve the penetration of the concrete by water or aqueous solutions. Therefore, it is concluded that concrete with low permeabilities are most likely to achieve service lives of around 500 years.

Some research has been carried out on predicting the service life of concrete based on the development of models. Models have been developed for predicting service lives of concrete exposed to corrosive conditions, freezing and thawing, and leaching by groundwater. These models appear to give at least semi-quantitative estimates of service lives. Further work on developing models is recommended. For example, a modeling

concept for predicting the service life of concrete exposed to sulfates is described.

It is concluded that, in developing an approach for predicting the service lives of concretes, with desired lives of 500 years, that accelerated testing should be combined with mathematical models. Accelerated tests should be developed following the procedures outlined in ASTM E 632 (5).

Although alkali-aggregate expansive reactions do not often cause structural failure, they pose a difficult problem. Present test methods are not adequate to predict the behavior of potentially reactive aggregates in field concrete. Furthermore, the present knowledge on alkali-aggregate reactions is inadequate for making service life predictions. It is recommended that a test method be developed for determining if an aggregate is potentially reactive.

The long-term performance of concrete is often controlled by the level of its quality. Based on available knowledge, it seems likely that concrete can be formulated which should have service lives of 500 years in the expected environments. However, such lives will be obtained only if the concrete materials meet carefully defined specifications, and good construction practices are followed. To assess this, an adequate QA/QC program must be established and faithfully implemented.

13. ACKNOWLEDGMENTS

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Appendix A: Barrier Systems for Protecting Concrete Surfaces

A1. BACKGROUND

Most of the major degradation processes of concrete involve the ingress of water or aqueous solutions into concrete. An approach for restricting the ingress of water is to cover the exterior concrete surfaces of a below-ground vault with a barrier material. Also, a barrier material applied to the inside concrete surfaces will assist in preventing nuclear waste materials from escaping a below-ground vault. An additional reason for applying barrier materials is to prevent movement of unwanted materials through cracks in the concrete (A1) or through joints. A detailed discussion of nonstructural cracks is given in reference A1.

Recommendations for general design criteria and specific design review criteria for the design, construction and operation of the below-ground vault alternative method of low level radioactive waste (LLW) disposal have been given by Denson et. al.(A2). Moisture barriers are also treated, including applicable tests, specifications, standards, and codes; coatings and sealers; sheet membranes; waterstops; joint sealants; bentonite panels; and a rationale for the moisture barrier recommendations.

The information in this appendix is considered supplementary to that by Denson et. al. (A2). For example, waterstops, geosynthetics, and bentonite panels are covered in reference A2, but not in this appendix. This appendix provides information primarily on asphalt, built-up membrane barriers for exterior below-ground vault surfaces and protective barrier systems for interior below-ground vault surfaces. Joint sealant materials are also briefly covered.

Barrier materials and joint sealants are intended to prevent the movement of liquid water and aqueous solutions and significantly reduce the passage of vapor from water or aqueous solutions into a building or through building elements, such as walls, roofs, and floors.

A2. EFFECTS OF RADIATION

The potentially detrimental effects of radiation on barrier materials, including asphalt and its reinforcement, sealants, and protection board may be an important factor in the selection of barrier materials and systems. For example, asphalt, a major component in conventional waterproofing barriers, can be degraded by gamma irradiation (A3). The chairman of ACI Committee 515 (Coatings for Concrete (A4)) expressed concern that

(i) conventional (i.e., not designed to resist radiation) waterproofing barrier systems and sealants may perform poorly when exposed to radiation and, (ii) that the effects of radiation on conventional barrier materials and sealants need to be taken into account in selecting barrier materials and sealants.

According to the chairman, there is no published information on the performance of waterproofing barrier systems for concrete exposed to radiation. An improved basis for selecting barrier materials and systems needs to be developed based on:

(i) an interpretation of published information on the effects of radiation on individual components of the barrier systems or materials similar to barrier materials,

(ii) analyses of field experience of the performance of barrier materials and systems at existing facilities exposed to radiation. Similarly, an improved basis for selecting sealants needs to be developed based on an interpretation of published information and field experience on the effects of radiation on sealants.

The authors recommend, in addition to the above, that accelerated durability testing should be carried out on (a) barrier materials and systems and, (b) sealants to form a basis for predicting their service lives.

Another factor which should be considered is the possibility of "self-heating" (A3) of the LLW resulting in unwanted thermal flow of the barrier materials or sealants.

Because of the lack of published information on the performance and service life of barrier systems and sealants for concrete exposed to radiation and a lack of knowledge of the dosage of radiation expected, the information presented herein is based on the performance of conventional barrier systems and sealants in the absence of radiation effects.

Therefore, if shown to be important, the effects of radiation, in addition to conventional degradation factors (moisture, acid, etc.) treated in this report, need to be taken into account when selecting barrier materials and sealants.

A3. TYPES OF CONVENTIONAL BARRIER SYSTEMS

Two types of conventional barrier systems for concrete surfaces (A5) appear applicable to the 500 year design-life LLW concrete burial vaults: waterproofing barrier systems and protective barrier systems. A waterproofing barrier system consists of a materials system applied to a concrete surface or structure and is intended to exclude liquid water and aqueous solutions and to significantly reduce the passage of vapor from water or aqueous

solutions. Examples of driving forces which can cause liquid or vapor movement include hydrostatic heads, vapor gradients, and capillary action. Porous concrete, cracks or structural defects, or joints that are improperly designed or constructed will increase the passage of liquids and vapors. A protective barrier system consists of a materials system applied to a concrete surface to protect the concrete from degradation by aqueous solutions or chemicals and a subsequent loss in its structural integrity.

A3.1 Waterproofing Barrier Systems

Reference A5 states that "Membrane waterproofing is the most reliable type of barrier to prevent liquid water under a hydrostatic head from entering an underground structure." Waterproofing barriers have traditionally consisted of multiple layers of bituminous-saturated felt or fabric cemented together with hot applications of coal tar pitch or asphalt. There are also cold-applied systems, which use multiple applications of asphaltic mastics and glass fabrics. Other cold-applied systems use liquids, sheet elastomeric materials, and preformed "rubberized bituminous" sheets (A5). References A5 and A6 give the details for the various hot-applied and cold-applied systems, including materials used, and factors relating to the interaction of the waterproofing barrier and the concrete surface

(surface preparation, adhesion, water accumulation at the interface, etc.). It is essential that there be good adhesion between the barrier membrane and the concrete to prevent water migration and leakage at the barrier-concrete interface due to unwanted cuts or openings in the barrier material.

The bitumens (asphalt or coal-tar pitch) used in hot-applied systems have very little strength themselves. They, therefore, need to be reinforced with fabrics or felts to withstand the stresses caused by temperature changes, expansion, contraction, vibration, and movement of the structure. Similarly, the mastic and emulsions used in the cold-applied systems do not have the necessary strength by themselves and need to be reinforced with fabric.

A3.2: Protective Barrier Systems

Protective barrier systems can be used to protect the concrete in the below-ground vault from degradation by aqueous solutions and chemicals from the LLW, which could permit the passage of LLW through the concrete. At the ambient service temperature, protective barrier materials should have the following basic properties to be effective in protecting the concrete from chemicals (A5):

- (a) the protective barrier material should not swell, dissolve, crack or embrittle upon contact with pertinent liquids or vapors;

(b) the barrier material should prevent the permeation or diffusion of chemicals which are able to cause a loss of adhesion between the barrier and the concrete; and

(c) the barrier material should have sufficient abrasion resistance to prevent it from being damaged during placement and maneuvering of the LLW containers in the vault. Brick sheathing applied over the barrier material (e.g., built-up asphalt membrane) is considered necessary to help prevent damage to the barrier material in those areas where barrier contact and potential damage is anticipated. For example, damage to the floor and perhaps the walls could occur due to cutting forces from mechanical action or cold-flow from sustained loading.

Reference A5 provides additional information, including factors which affect the adhesion of the protective barrier to the concrete, and also the effects of the concrete structure (e.g., cracks in the concrete reflecting through the barrier) and foundation movements on the performance of the protective barriers.

A4. DEGRADATION FACTORS AND SERVICE LIFE PREDICTION OF BARRIER MATERIALS

Various degradation factors can affect the ability of the barrier (waterproofing and protective) materials and sealant materials to

perform properly over the required design life of 500 years. The factors anticipated include chemical attack; oxygen, if it is available underground; moisture; alkalies; acids; biological species (e.g., microorganisms, insects, and plant and tree roots); radiation (from LLW); structural movement, including settlement, which induces strains; sustained loading from the LLW, which can cause cold-flow of the barrier material beneath the LLW; and cutting forces occurring during placement of the LLW into the below-ground vault. The effects of these degradation factors would depend on their severity and their duration of occurrence during the life of the structures.

In addition, prior to burial, the barrier materials and sealant materials may be exposed to ultraviolet light, ozone, temperature cycling, increased temperature (e.g., caused by sunlight, which could result in unwanted flow in an asphalt barrier) and other forms of weathering. The effect of these degradation factors would depend on the severity and duration of exposure prior to burial.

There are a number of reports which provide information on the effects of various conventional degradation factors, as well as radiation, on the properties of polymers and bituminous and asphaltic materials (see, for example, references A3 and A7 to A17).

ASTM E 632 (A18), can be used as a guide in developing a methodology for predicting the service life of the barrier materials and sealant materials exposed to various degradation factors as described above. Accelerated tests may need to be used but care must be taken to insure that the degradation mechanisms induced by the tests and the in-service environment are the same. Appropriate physical and mechanical properties which are sensitive to changes in the performance of the barrier materials and sealant materials when exposed to the anticipated environment need to be identified. For example, moisture permeability could be one of the most important properties. Consideration should be given to moisture permeability tests which simulate, as closely as possible, the in-service conditions. For example, with a built-up membrane barrier, the configuration of the membrane (plies etc.) and how it would be applied to the concrete surface should be simulated by the tests, as close as possible.

A possible source of information on the performance and durability of barrier materials and sealant materials would be to examine the condition of waterproofing barriers and sealants of older buried structures for which records are available on their age and on the types of materials used. Examples of potential structures include facilities exposed to radiation, cemetery burial vaults, basement walls of residences, foundations of buildings and structures, underground storage structures, and

transportation facilities. Similarly, the performance and durability of protective barrier materials and sealant materials in existing structures may provide information useful in predicting their service lives.

A4.1 Conventional Waterproofing and Protective Barrier Materials

Potential conventional barrier materials are discussed based on limited existing information, excluding the potentially detrimental effects of radiation (see Sections A2 and A5).

Long term performance is considered to be the most important criterion for selecting candidate materials for below-ground vaults. Hence, materials with a history of performance of 500 years or more are preferred. The historical use of bituminous materials has been documented (see below). Before World War II, most of the commercial polymeric materials occurred naturally (A19). Hence, the use of synthetic polymers has no long-term performance records relative to the required 500 year design life. Even the bituminous materials do not have detailed performance records concerning their physical and mechanical properties, which would verify that they would perform properly under specified degradation factors for 500 years. None-the-less, because they have been documented historically, asphalt built-up membranes should be considered for possible use as a waterproofing barrier on the exterior of the below-ground vault.

A protective barrier system applied to the inside of the below-ground vault, consisting of an asphalt built-up membrane covered by brick sheathing, should also be considered, provided the asphalt membrane has adequate chemical resistance. (Regardless of the membrane, brick sheathing applied over the protective barrier membrane material is considered necessary to help prevent damage to the barrier material in those areas where barrier contact and potential damage is anticipated - see Section A3.2).

If an asphalt membrane (applied on the interior of the below-ground vault) does not have adequate resistance against chemical attack resulting from the LLW inside the below-ground vault, then other types of protective barrier materials and systems need to be considered. For example, if concentrated acids or acid/solvent combinations are anticipated from the LLW, use of an asphalt membrane (other membranes may be used depending on the chemical environment) combined with masonry construction consisting of "acid-proof" brick using a chemical-resistant mortar (A5) should be considered.

Additional discussion of the design and selection of chemically resistant masonry materials is given in references A20 and A21. For conventional barriers, fiberglass fabric or felt reinforcement in the asphalt membrane is believed to be more durable than other reinforcement, provided the fiberglass binders are water resistant.

Barrier systems containing asphalt are believed to be candidate conventional systems because of the documented longevity of asphalt for a variety of ancient applications (A22). For example, Abraham (A22) states with regard to a Pleistocene Cypress tree trunk recovered from the Rancho-la-Brea asphalt pits in California and preserved by asphalt for 25000 years: "This represents one of the oldest specimens of wood in existence and bears mute evidence of the remarkable preservation properties of asphalt." Abraham documents a number of cases of the use of asphalt mortar or asphalt mastic in ancient times. For example, with regard to the use of asphalt with bricks (about 2200 B.C.), Abraham quotes: "Robert Koldewey reports that when excavating in Babylon, he found that 'it was exceedingly difficult to separate the brick courses from each other.' This was also confirmed by A. H. Layard, who states that 'Bricks bonded with asphalt have remained immovably in place for thousands of years.'" Abraham also states, with regard to King Nebuchadnezzar (604 to 561 B.C.), that burnt bricks bearing the name of Nebuchadnezzar "were laid in asphalt, and are still so firmly jointed together today, that it is impossible to part them without destroying their integrity."

A4.2 Conventional Sealant Materials

Use of joints should be minimized as the performance of joint-sealant materials is often a troublesome problem (A23, A24, A25).

Joint design, sealant selection, and installation are treated in references A23 and A24. Conventional, synthetic, polymeric sealants have an estimated maximum service life of about 20 to 40 years (about 20 to 30 years for urethanes and polysulfides and 30 to 40 years for high-modulus silicones (A26)). High-modulus silicones have been used since the 1950's and may have service lives in excess of 40 years. These high-modulus silicones have very little plasticizer to migrate out and cause hardening (A26). Medium-modulus silicones have been used for about 25 years and are currently replacing the high-modulus silicones because of the greater movement capability of the medium-modulus silicones (A26). The effect of radiation from LLW on the service life of the sealants also needs to be considered (Sections A2 and A5). Thus, it appears that the sealant materials could be at least as critical as the waterproofing barrier materials, since the synthetic, polymeric sealants have a documented service life of only about 20 to 40 years compared to the required service life of 500 years.

A4.3 Design Considerations for Conventional Materials

To prevent their failure, the interior and exterior barriers of the below-ground vault must be designed to accommodate movement at the joints. Furthermore, if for any reason an exterior or interior barrier fails, liquid or vapor could migrate at the

barrier-concrete interface until reaching a point of low resistance to passage, which most likely would be at joints (and their sealant materials), or at unwanted cracks in the concrete. Thus, if a barrier system fails, the sealant materials could then become a critical element in the prevention of unwanted liquids and vapors moving through the vault. Therefore, (i) the use of joints should be minimized, (ii) penetrations through the concrete or the barrier systems or both should be eliminated, (iii) proper design is needed to insure that the barriers are able to move (rather than fail) as the joints move and, (iv) systems with redundant waterproofing barrier systems or redundant concrete elements or both should be considered in designing an impervious structure.

The use of protection board covering should be considered to protect the exterior barrier from being damaged (e.g., when performing work on, near, or over the barrier, and when backfilling the barrier; see Part 1, IV, A. "Protection Courses," reference A6). In addition, the use of brick sheathing should also be considered to protect the interior protective barrier system in those areas where barrier contact and damage is anticipated (see Section A3.2).

A5. RESEARCH NEEDS

Very little is known about the long-term service life of barrier materials and systems and sealant materials, including the effects of radiation. A methodology, using ASTM E 632 (A18) as a guide, needs to be developed to predict the service lives of potential barrier systems and sealant materials, when exposed to conventional degradation factors (moisture, acids, etc.) as well as radiation.

The extent of potential degradation by radiation of barrier systems and sealant materials depends on the dosage of the radiation. The dosage of radiation to which barrier materials are likely to be exposed should be determined.

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APPENDIX B. SOME COMMON CHEMICALS AND SUBSTANCES AGGRESSIVE TO
PORTLAND CEMENT CONCRETE

Table B1. Inorganic Chemicals and Substances^{1,2}

Distilled water

Soft water

Acids:	Bromic acid Hydrochloric acid Hydroflouric acid Nitric acid Sulfuric acid	Carbonic acid Chromic acid Hydrogen sulfide Phosphoric acid Sulfurous acid
Bases:	Sodium hydroxide	Potassium hydroxide
Salts:	Chlorides (Ca, Na, NH ₄ , Mg) ³ Sulfates (Al, Ca, Fe, Cu, K, Mg, Na, NH ₄) Nitrates and nitrites (Na, K, NH ₄) Sulfides (Fe, Na) Sulfites and bisulfites (Na) Acetates (Ca, Al, NH ₄)	
Gases:	Carbon dioxide Chlorine Sulfur dioxide	
Others:	Sodium thiosulfate Sodium borate (borax) - small effect.	

¹Durability of Concrete Structures, CEM-RILEM International Workshop, May 1983.

²F.M. Lea, The Chemistry of Cement and Concrete, 3rd ed. (Chemical Publishing Co., N.Y., 1970).

³Common cations.

Table B2. Organic Chemicals and Substances^{1,2}

Acids:	Acetic acid	Butyric acid
	Citric acid	Formic acid
	Humic acid	Lactic acid
	Malic acid	Tannic acid
	Uric acid	

Alcohols:	Ethanol	Methanol
	Phenol	Propanol
	Glycerol (glycerine)	

Amines

Esters

Stearates: Glyceryl sterate (stearin)

Sugar solutions

Vegetable oil and animal oil - contain fatty acids:

Oleic acid
Stearic acid
Palmitic acid

¹Durability of Concrete Structures, CEB-RILEM International Workshop, May 1983.

²F.M. Lea, The Chemistry of Cement and Concrete, 3rd ed. (Chemical Publishing Co., N.Y., 1970).

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<p>10. SUPPLEMENTARY NOTES</p> <p><input type="checkbox"/> Document describes a computer program; SF-185, FIPS Software Summary, is attached.</p>			
<p>11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here) The U.S. Nuclear Regulatory Commission (NRC) has the responsibility for developing a strategy for the disposal of low-level radioactive waste (LLW). An approach being considered for their disposal is to place the waste forms in concrete vaults buried in the earth. A service life of 500 years is required for the concrete vaults as they may be left unattended for much of their lives.</p> <p>This report examines the basis for making service life predictions based on accelerated testing and mathematical modeling of factors controlling the durability of concrete buried in the ground. Degradation processes are analyzed based on considerations of their occurrence, extent of potential damage, and mechanisms. A recommended research plan for developing methods for predicting the service life of concrete is presented.</p> <p>The major degradation processes that concrete of underground vaults will likely encounter are sulfate attack, corrosion of reinforcing steel, alkali-aggregate reactions and leaching by ground water. Freezing and thawing damage could occur before the vaults are covered with soil and therefore are addressed. Other degradation processes which may occur are microbiological attack, salt crystallization, and attack by LLW, especially by acidic materials. Two important factors controlling the resistance of concrete to these degradation processes are its quality and permeability. Concepts of quality and factors affecting quality of concrete are discussed. Permeability is discussed in terms of the water-to-cement ratio, the pore structure of concrete, and the effects of cracks.</p>			
<p>12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)</p> <p>Accelerated testing; alkali-aggregate reactions; concrete; corrosion; durability; groundwater; mathematical modeling; permeability; service life; sulfate attack</p>			
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